VOL. XLII 1922

TRANSACTIONS of the American Electrochemical Society

VOLUME

LIBRARY

BRIGHAM YOUNG UNIVERSITY

FROM H. H. Smith

CALL NO [redacted] ACC. NO. 25570

PERIODICAL

Group at St. James Cathedral, Montreal, Que., September 22, 1922

TP
250
.E542

TRANSACTIONS

OF THE

American Electrochemical Society

PRINCETON UNIVERSITY
LIBRARY
PROPERTY OF

VOLUME XLII

FORTY-SECOND GENERAL MEETING

MONTREAL, QUE., CANADA

SEPTEMBER 21, 22 AND 23, 1922

PUBLISHED BY

The American Electrochemical Society

AT THE OFFICE OF THE SECRETARY

COLUMBIA UNIVERSITY, NEW YORK CITY

1923

Copyright 1923 by the American Electrochemical Society.

Permission to reprint parts of the *Transactions* is hereby granted to current periodicals, provided due credit is given.

This Society is not responsible for the statements and opinions advanced in papers or in discussion thereon.

Prices of Volumes I to XLII (excepting Vols. I, II, III, VII, XXIX and XXXI), to non-members $6.50 per copy; to members, $2.50; to public libraries, colleges, scientific societies and journals, $4.00. Volumes I, II, III, VII, XXIX and XXXI, double above prices. Prices are for volumes bound in cloth, and include delivery within the postal union.

When the stock of any volume has been reduced to 25 copies (as Vol. III), the sale is limited to those purchasing the given volume as part of a complete set.

Complete sets will be sold to anybody at 25 percent discount on above prices; members may obtain the volumes necessary to complete their sets at 25 percent reduction on above prices.

WARE BROS. COMPANY, PRINTERS
1010 ARCH ST., PHILA.

OFFICERS OF THE SOCIETY

PRESIDENT

C. G. SCHLUEDERBERG
Term expires 1923

PAST-PRESIDENT

ACHESON SMITH
Term expires 1923

VICE-PRESIDENTS

C. F. BURGESS
J. A. MATHEWS
E. L. CROSBY
Terms expire 1923

H. C. PARMELEE
A. H. HOOKER
W. S. LANDIS
Terms expire 1924

MANAGERS

G. K. ELLIOTT
H. B. COHO
F. J. TONE
Terms expire 1923

CARL HERING
J. V. N. DORR
F. A. J. FITZ GERALD
Terms expire 1924

A. T. HINCKLEY
W. M. CORSE
WM. BLUM
Terms expire 1925

TREASURER

F. A. LIDBURY
Term expires 1923

SECRETARY

COLIN G. FINK, Columbia University, New York City
Term expires 1923

COMMITTEES

PUBLICATION COMMITTEE

F. A. J. FITZGERALD, Chairman

COLIN G. FINK, *Ex Officio*
WM. BLUM
C. B. GIBSON
Terms expire 1923

C. G. SCHLUEDERBERG, *Ex Officio*
A. T. HINCKLEY
H. C. PARMELEE
Terms expire 1924

COMMITTEES—Continued

COMMITTEE ON LOCAL SECTIONS

F. J. Tone, Chairman — Colin G. Fink — C. G. Schluederberg

PATENT COMMITTEE

L. H. Baekeland, Chairman — F. G. Cottrell — E. J. Prindle

PUBLIC RELATIONS COMMITTEE

C. G. Schluederberg, Chairman

W. D. Bancroft
Carl Hering
C. F. Burgess
E. G. Acheson
L. H. Baekeland
W. H. Walker
W. R. Whitney
F. A. Lidbury
Lawrence Addicks
F. A. J. FitzGerald
Colin G. Fink
F. J. Tone
W. S. Landis
Acheson Smith

MEMBERSHIP COMMITTEE

A. T. Hinckley, Chairman

M. DeK. THOMPSON, Cambridge, Mass.
L. E. SAUNDERS, Worcester, Mass.
G. B. HOGABOOM, Waterbury, Conn.
H. C. PARMELEE, New York, N. Y.
C. F. ROTH, New York, N. Y.
E. F. KERN, New York, N. Y.
J. A. SEEDE, Schenectady, N. Y.
H. W. GILLETTE, Ithaca, N. Y.
G. H. CLAMER, Philadelphia, Pa.
R. E. ZIMMERMAN, Pittsburgh, Pa.
D. A. LYON, Washington, D. C.
P. J. KRUESI, Chattanooga, Tenn.
THEODORE SWANN, Anniston, Ala.
L. A. DREFAHL, Cleveland, O.
T. F. BAILY, Alliance, O.
G. K. ELLIOTT, Cincinnati, O.
W. K. BOOTH, Chicago, Ill.
O. P. WATTS, Madison, Wis.
E. L. CROSBY, Detroit, Mich.
J. W. BECKMAN, Oakland, Cal.
C. E. WILLIAMS, Seattle, Wash.
F. T. KAELIN, Montreal, Canada.
J. T. BURT-GERRANS, Toronto, Can.
J. G. BUTTERS, Hobart, Tasmania.
F. ANDERSEN, Trollhattan, Sweden.
HANS LANDOLT, Turgi, Switzerland.
B. BERG-HANSEN, Christiania, Norway.
K. B. QUINAN, W. Somerset, Cape Province, S. Africa.
C. A. KELLER, Paris, France.
H. E. ETCHELLS, Sheffield, England.
F. GIOLITTI, Torino, Italy.
YOGORA KATO, Tokio, Japan.
JEN CHOW, Shanghai, China.

WAYS AND MEANS COMMITTEE

H. B. Coho, Chairman

Lawrence Addicks
Colin G. Fink
Carl Hering
F. A. Lidbury
H. C. Parmelee

DIVISIONS OF THE SOCIETY

ELECTROTHERMIC DIVISION

Bradley Stoughton, Chairman

J. A. Mathews, Vice-Chairman — Colin G. Fink, Secretary-Treasurer

Directors

G. K. Elliott
James H. Parker
W. J. Priestley
Dorsey A. Lyon

DIVISIONS OF THE SOCIETY—Continued

ELECTRODEPOSITION DIVISION

GEORGE B. HOGABOOM, Chairman

CHAS. S. WITHERELL, Vice-Chairman WM. BLUM, Secretary-Treasurer

Directors

LAWRENCE ADDICKS F. C. MATHERS
E. F. KERN O. P. WATTS

Foreign Representatives

W. E. HUGHES,
Seaford, England

BERTRAM WOOD,
Hobart, Tasmania

TECHNICAL COMMITTEES

PRIMARY BATTERIES

C. F. BURGESS, Chairman D. L. ORDWAY

SECONDARY BATTERIES

P. G. SALOM, Chairman O. W. BROWN

ELECTRO ANALYSIS

H. S. LUKENS, Chairman GEO. S. FORBES

RADIO ACTIVITY

S. C. LIND, Chairman H. S. MINER

CHLORINE AND CAUSTIC

E. M. SERGEANT, Chairman HUGH K. MOORE L. D. VORCE

CORROSION

COLIN G. FINK, Chairman W. M. CORSE W. D. RICHARDSON

FIXED NITROGEN

W. S. LANDIS, Chairman ARTHUR B. LAMB FRANK S. MCGREGOR

WATER POWER

J. H. HARPER, Chairman J. L. YARDLEY H. J. PIERCE

ORGANIC ELECTROCHEMISTRY

C. J. THATCHER, Chairman ALEXANDER LOWY

ELECTROCHEMISTRY OF GASEOUS CONDUCTION

DUNCAN MACRAE, Chairman WM. R. MOTT

INSULATING OILS AND VARNISHES

H. C. P. WEBER, Chairman

C. D. HOCKER C. J. RODMAN

CHRISTIAN DANTSIZEN

LOCAL SECTIONS OF THE SOCIETY

Philadelphia Section

CARL HERING, Chairman, Philadelphia, Pa.
S. S. SADTLER, Secretary, Philadelphia, Pa.

New York Section

H. C. COOPER, Chairman
P. D. MERICA, Vice-Chairman
P. D. V. MANNING, Secretary-Treasurer

Pittsburgh Section

EARL BLOUGH, Chairman, New Kensington, Pa.
C. B. GIBSON, Secretary-Treasurer, Pittsburgh, Pa.

Niagara Falls Section

E. M. SERGEANT, Chairman, Niagara Falls, N. Y.
W. A. MCKNIGHT, Secretary and Treasurer, Niagara Falls, N. Y.

TABLE OF CONTENTS

PAGE

Group at St. James Cathedral, Montreal, Quebec.....Frontispiece
Proceedings of the Forty-second General Meeting..... 1
Members and Guests Registered at the Forty-second General Meeting.. 5

PAPERS.

Effect of Heat Treatment on the Hardness and Microstructure of Electrolytically Deposited Iron—Norman B. Pilling..... 9
The Preparation and the Mechanical Properties of Vacuum-fused Alloys of Electrolytic Iron with Carbon and Manganese—Robert P. Neville and John R. Cain..... 21
The Dezincification of Brass—Ralph B. Abrams..... 39
Electroplated Zinc and the Diffusion of Electrodeposits into Zinc—Walter G. Traub 55
The Effect of Single Impurities on the Electrodeposition of Zinc from Sulphate Solutions—John T. Ellsworth 63
The Effect of Impurities in Nickel Salts Used for Electrodeposition—M. R. Thompson and C. T. Thomas..... 79
The Application of Contractometer to the Study of Nickel Deposition —E. A. Vuilleumier 99
Electric Heat, Its Generation, Propagation and Application to Industrial Processes—E. F. Collins 113
Principles of High Temperature Furnace Design—E. L. Smalley.....147
Some Electrical Properties of Alloys at High Temperatures—M. A. Hunter and A. Jones 159
Resistivities of Some Granular Resistor Carbons—Clyde E. Williams and Gordon R. Shuck 181
The Development of Industrial Electric Heating for Low Temperature Enameling—Wirt S. Scott 195
Firing of Ceramics in Electric Furnaces—E. L. Smalley.....209
Electric Steam Generators and their Application—P. S. Gregory.....215
A New Induction Furnace—J. Murray Weed 233
A Simple Electric Crucible Furnace for Melting Aluminium—A. Glynne Lobley 249

PAGE

Manufacture of Carbon Bisulphide—George A. Richter 253

Electrosmosis and Electrophoresis, Two Definitions—Oliver C. Ralston.269

Electrolytic Oxidation of Isoeugenol—Alexander Lowy and Catherine M. Moore 273

Preparation of Perchlorates by Heating Chlorates—Frank C. Mathers and Jacob W. H. Aldred 285

Changes in the Electrical Conductivity of Varnishes During Drying—H. C. P. Weber 293

Arc Action on Some Liquid Insulating Compounds—C. J. Rodman....305

VOLUME XLII 1922

TRANSACTIONS

OF THE

American Electrochemical Society

PROCEEDINGS

CONDENSED MINUTES AND RECORD OF THE FORTY-SECOND GENERAL MEETING OF THE SOCIETY, HELD IN MONTREAL, CANADA, SEPTEMBER 21, 22 AND 23, 1922.

The total registration at this meeting was 210, of whom 75 were members and 135 guests.

PROCEEDINGS OF WEDNESDAY, SEPTEMBER 20

The registration of delegates to the forty-second General Meeting of the Society began at 6.00 P. M. in the Windsor Hotel, Montreal.

PROCEEDINGS OF THURSDAY, SEPTEMBER 21

The Society members and guests gathered in the assembly hall of the Windsor Hotel at 10.00 A. M. President Schluederberg called the meeting to order and in a few words of introduction congratulated the members of the Society in selecting Montreal, one of the largest and oldest cities on the continent, as a meeting place. He then introduced Alderman Seybolt, who, on behalf of Mayor Mortan, welcomed the members of the Society and called attention to the many interesting parts of Montreal which were well worth while seeing. Additional words of welcome and greeting were most fittingly conveyed by Dr. R. F. Ruttan, past president of the Society of Chemical Industry, who, on behalf of the chemists of Canada, expressed every good wish for a success-

ful meeting. In recounting the rapid strides and progressive developments being made in the sciences of chemistry, electrochemistry and photochemistry, Dr. Ruttan in part spoke as follows:

"The American Electrochemical Society is one of those societies which has been stigmatized as being hybrid, as being a hyphenated scientific society; but these are the branches of science which are today the most effective; it is along the borderland between the great recognized branches of science, where the footing seems safest and strongest for advancement, and where the greatest progress is being made.

"In physical chemistry with its various branches of thermochemistry, photochemistry and electrochemistry, we find that progress is far more rapid than it is in the recognized branches of chemistry known as the old inorganic and organic chemistry."

Upon thanking Alderman Seybolt and Dr. Ruttan for their inspiring words of welcome, President Schluederberg called for the presentation of papers on electrolysis by the following authors: Norman B. Pilling, R. P. Neville and J. R. Cain, Ralph B. Abrams, Walter G. Traub, John T. Ellsworth, M. R. Thompson and C. T. Thomas, E. A. Vuilleumier. Papers by these authors are printed in full in these Transactions.

At noon the Board of Directors of the Society met for the purpose of transacting Society business. This meeting was continued in the afternoon following the reading and discussion of papers on "Industrial Heating by Electricity" by the following: E. F. Collins, E. L. Smalley, M. A. Hunter and A. Jones, C. E. Williams and G. R. Shuck, J. C. Woodson,* Wirt S. Scott. With the exception of the last two authors' papers: "Heat Insulating Materials for Electric Heating Apparatus" and "Advantages of Industrial Electric Heating" respectively, all papers with related discussion are printed in subsequent pages of this volume.

At 8.00 P. M. the members and guests assembled in the lecture room of the MacDonald Physics Building, McGill University, where Dr. A. S. Eve, a physicist of world-wide repute, delivered a most interesting address on "The New Philosophy of Physics." Dr. Eve outlined that his subject matter would deal with space, simply space in the abstract. He briefly related the history begin-

* Paper by J. C. Woodson in Vol. 43, these Transactions.

ning with the experiments of Sir Isaac Newton and followed up by the studies of James Clerk Maxwell, Lord Kelvin, Galilei and other eminent physicists. After explaining the difficulty gravitation is causing in the study of space, Dr. Eve turned attention to the subject of electricity. His experiments were exceptionally well carried out, and were received with great enthusiasm and appreciation by those in attendance. At the close of the lecture and upon motion by Secretary Fink, a rising vote of thanks was conveyed to Dr. Eve for the very delightful evening.

PROCEEDINGS OF FRIDAY, SEPTEMBER 22

At 10.00 A. M. the meeting convened for the purpose of reading and discussing papers by the following authors, being a continuation of the "Industrial Heating" Symposium of Thursday afternoon: Frank W. Brooke,* Wirt S. Scott, E. L. Smalley, P. S. Gregory, J. Murray Weed, A. Glynne Lobley. These papers, excepting the one by Frank W. Brooke, which was presented in abstract, are appended to these Proceedings.

Commencing at 2.30 P. M. discussion of papers on various electrochemical topics was continued. These papers, as presented and published in these Transactions, are by the following authors: Geo. A. Richter, Oliver C. Ralston, Alexander Lowy and Catherine M. Moore, F. C. Mathers, H. C. P. Weber, C. J. Rodman.

SOCIAL FEATURES

In the way of recreation and inspection trips through industrial plants there were abundant opportunities. Golf enthusiasts spent a number of delightful hours at the Kanawaki and Royal Montreal Golf Clubs. Visits to industrial plants (a list of which appears in the "Resolution of Thanks" in succeeding pages) in and around Montreal were arranged for by members of the local committee. In fact so many interesting functions had been planned for the visiting members of the Society that it was difficult to take in even a small fraction of these. The success of the meeting was to a large extent due to the untiring efforts and efficient management of the local committee, headed by Messrs. H. W. Matheson, of the Canadian Electroproducts Co., and C. R. Hazen, of the Milton Hersey Co. Mr. A. R. McLean had charge of the excursions,

* Paper by Frank W. Brooke in Vol. 43 of these Transactions.

and Mr. W. B. Woodland took care of the "publicity." It was largely due to Mr. Woodland's efficient methods that the convention was so well advertised and in consequence well attended.

An old-fashioned smoker was the feature of Friday evening, which afforded excellent opportunities for bringing old acquaintances together and for making new ones. Included in the program were talks by Mr. F. A. Lidbury on the "Contactometer," and Professor W. D. Bancroft on "Blues." For his excellent smoker discourse Dr. Bancroft was awarded the "Pickles Medal." Others who assisted in the entertainment were Henry Howard, L. E. Saunders, H. C. Parmelee, R. F. Ruttan, Robert Turnbull, and E. L. Crosby.

One of the most enjoyable and attractive features of the entire program was the trip to Shawinigan Falls. Special coaches, reserved for the Society, were attached to the midnight train arriving at the Falls early Saturday morning. Local members under the most able leadership of Mr. R. A. Witherspoon gave the visitors a cordial reception. From the Inn, as headquarters, trips were made by automobile to the following plants: Belgian Industrial Co., Canada Carbide Co., Laurentide Pulp and Paper Co., Shawinigan Water and Power Co.

The visiting ladies were most lavishly entertained by the ladies' local committee, Mrs. C. R. Hazen, Chairman.

At the conclusion of the session for the reading and discussion of papers Friday afternoon, Dr. Hering offered the following resolution of thanks which was heartily endorsed by a rising vote:

RESOLUTION OF THANKS

In closing its forty-second General Meeting at Montreal, the American Electrochemical Society wishes to record its very great appreciation of the assistance and co-operation cordially extended to its members and guests by the following persons and organizations:

The Local Committee in general charge of arrangement, particularly its efficient chairman, Mr. H. W. Matheson, whose untiring efforts contributed much to the success of the meeting.

The chairmen of the Golf Committee, the Excursion Committee,

the Smoker Committee and the Publicity Committee for their kind co-operation.

The Ladies' Committee, particularly Mrs. C. R. Hazen, chairman, for their care of visiting ladies.

The Canada Cement Co., St. Lawrence Sugar Refining Co., Imperial Oil Co., Dominion Engineering Works, Frontenac Breweries, Ltd., who so kindly opened their plants to inspection.

The Kanawaki and Royal Montreal Golf Clubs for the generous tendering of the use of their grounds and facilities to our members and guests.

The management of the Windsor Hotel for the facilities for holding our technical sessions, and for the use of a special room for registration purposes.

MEMBERS AND GUESTS REGISTERED AT THE FORTY-SECOND GENERAL MEETING

Members.

Geo. P. Adamson
A. G. Ahrens
R. O. Bailey
Wilder D. Bancroft
P. McN. Bennie
Wm. Blum
Frank W. Brooke
Fred E. Carter
E. F. Collins
E. F. Cone
W. M. Corse
Wm. A. Cowan
E. L. Crosby
R. W. Davis, Jr.
Wm. Delage
W. H. Falck
P. H. Falter
Colin G. Fink
F. A. J. FitzGerald
Wm. H. Gesell
C. B. Gibson
J. B. Glaze
Anton Gronningsater
Fred. J. Hambly
W. G. Harvey
Carl Hering
A. T. Hinckley
Henry Howard
M. A. Hunter
F. A. Lidbury
E. A. Lof
Alexander Lowy
Dorsey A. Lyon
D. McIntosh
Robert J. McKay
John McLeish
Duncan MacRae
R. G. Mansfield
H. W. Matheson
Dwight D. Miller
W. Lash Miller
H. C. Parmelee
A. G. Reeve
A. E. Rhoads
George A. Richter
F. W. Robinson
C. J. Rodman
Daniel B. Rushmore
L. E. Saunders
C. G. Schluederberg
Wirt S. Scott
J. A. Seede
George N. Sieger
Acheson Smith
Walter S. Smith
H. W. Spicer
A. D. Spillman
Alfred Stansfield
E. Takagi
L. S. Thurston
Robert Turnbull
F. M. Turner, Jr.
M. Unger
Mary U. von Isakovics
Frank J. Vosburgh
F. S. Weiser
Archie J. Weith
P. L. Westman
A. W. Whitaker, Jr.
H. M. Williams
A. M. Williamson
Edwin L. Willson
J. Rattray Wilson
R. A. Witherspoon
J. L. M. Yardley

Guests.

H. G. Aires, Niagara Falls, N. Y.
J. D. Alley, Wilkinsburgh, Pa.
Dennis Baker, Montreal, Canada
Mrs. W. D. Bancroft, Ithaca, N. Y.
Miss Bancroft, Ithaca, N. Y.
Mrs. C. F. Bardorf, Montreal, Canada.
John S. Bates, Bathurst, N. B.
G. E. Baughman, Montreal, Canada.
Leon Beauchamp, Montreal, Can.
Mrs. Jerome B. Bell, Montreal, Canada.
J. W. Bell, Montreal, Canada.
Q. E. Bell, Montreal, Canada.
H. M. Biebel, Oakmont, Pa.
W. O. Birton, Montreal, Canada.
W. D. Bishop, Montreal, Canada.
H. E. Bokken, Niagara Falls, N. Y.
A. F. Braid, New York City.
Mrs. A. F. Braid, New York City.
E. Brown, Montreal, Canada.
H. A. Buddow, Montreal, Canada.
R. M. Burns, New York City.
W. P. S. Cam, Montreal, Canada.
Gus Campbell, Niagara Falls, N. Y.
H. M. Campbell, Montreal, Canada.
Mrs. Fred E. Carter, Newark, N. J.
W. B. Cartnul, Montreal, Canada.
H. A. Caveni, Ottawa, Canada.
Mrs. H. A. Caveni, Ottawa, Canada.
Mrs. George Chadwick, Niagara Falls, N. Y.
C. V. Christie, Montreal, Canada.
Ingeborg Clementson, Montreal, Canada.
M. C. Clementson, Montreal, Can.
Bernard Collett, Montreal, Canada.
Mrs. E. L. Crosby, Detroit, Mich.
S. Cunha, Montreal, Canada.
J. B. Darling, Detroit, Mich.
E. B. Davidson, Montreal, Canada.
Wallace Dickson, Montreal, Canada.
J. Dolid, Montreal, Canada.
J. T. Donald, Montreal, Canada.
P. I. Donald, Montreal, Canada.
F. L. Driver, Jr., Newark, N. J.
Horace Driver, Philadelphia, Pa.
A. R. Dufresni, Montreal, Canada.
Albert Dupuis, Montreal, Canada.
W. H. Eastlake, Montreal, Canada.
R. W. Erwin, Flushing, N. Y.
Mrs. Irving Fellner, Rye, N. Y.
Irving Fellner, New York City.
Mrs. Colin G. Fink, S. Yonkers, N. Y.
C. M. FitzGerald, New York City.
Mrs. C. M. FitzGerald, New York City.
Mrs. F. A. J. FitzGerald, Niagara Falls, N. Y.
A. G. Fleming, Montreal, Canada.
D. M. Gall, Montreal, Canada.
G. R. Hale, Shawinigan Falls, Can.
Jos. Haynes, Montreal, Canada.
Chas. R. Hazen, Montreal, Canada.
Mrs. Chas. R. Hazen, Montreal, Canada.
Chas. E. Herd, Montreal, Canada.
Otto W. Herzberg, Montreal, Can.
Q. J. C. Heurer, Montreal, Canada.
Katharine Howard, Cleveland, Ohio
Geo. M. Hudson, Montreal, Canada.
H. L. Humes, Montreal, Canada.
Robert Job, Montreal, Canada.
Fraser Q. Keith, Montreal, Canada.
H. C. Kennedy, Montreal, Can.
Wm. Kennedy, Jr., Montreal, Can.
D. H. Killefer, New York City.
Louis V. King, Montreal, Canada.
E. O. Kirkpatrick, Montreal, Can.
P. P. Labelle, Montreal, Canada.
J. D. Lachapelle, Montreal, Canada.
R. S. Lea, Montreal, Canada.
L. McCoy, Montreal, Canada.
M. C. Coll McFee, Montreal, Can.
H. C. Mabee, Ottawa, Canada.
J. R. Macaulay, Montreal, Canada.
A. M. Mackenzi, Montreal, Canada.
A. R. M. MacLean, Montreal, Can.
L. H. Marrotte, Montreal, Canada.

Chas. F. Medbury, Montreal, Can.
R. W. Milnes, Kenwood, N. Y.
N. L. Morgan, Montreal, Canada.
Ed. H. Morley, Montreal, Canada.
W. P. Muir, Montreal, Canada.
George E. Neuill, Montreal, Canada.
R. Nishikawa, Japan.
J. W. O'Brien, Cleveland, Ohio.
Fred. E. O'Neill, Niagara Falls, N. Y.
Alexander Peden, Montreal, Can.
A. I. Peterson, Montreal, Canada.
Geo. Philips, Montreal, Canada.
Norman B. Pilling, East Pittsburgh, Pa.
R. Prefontaine, Montreal, Canada.
H. K. Richardson, Newark, N. J.
A. M. Ritchie, Montreal, Canada.
F. A. Ritchie, St. Lambert, Can.
Harold J. Roast, Montreal, Canada.
Mrs. F. W. Robinson, Newark, N. J.
R. F. Ruttan, Montreal, Canada.
S. S. Sach, Montreal, Canada.
Mrs. Carl G. Schluederberg, East Pittsburgh, Pa.
W. E. Scott, Montreal, Canada.
T. P. G. Shaw, Montreal, Canada.
F. W. Skirrow, Shawinigan Falls, Canada.
Mrs. Acheson Smith, Niagara Falls, N. Y.
A. G. Spencer, Montreal, Canada.
Gordon Sproule, Montreal, Canada.
R. E. Stavert, Montreal, Canada.
Earl P. Stevenson, Cambridge, Mass.
A. C. Taggi, Montreal, Canada.
L. O. Thomas, Ottawa, Canada.
Phillips Thompson, Cleveland, Ohio.
Norman Tice, Waterbury, Conn.
R. J. Traill, Ottawa, Canada.
Mrs. R. Turnbull, Niagara Falls, N. Y.
Mrs. F. M. Turner, Jr., New York City.
E. J. Turnley, Westmont, Canada.
W. Stanley Vipond, Montreal, Can.
Miss von Isakovics, Monticello, N. Y.
H. H. Vroom, St. Lambert, Canada.
L. J. Waldbauer, Montreal, Canada.
R. M. Walker, St. Lambert, Canada.
Wm. A. Wardwell, Montreal, Can.
H. C. P. Weber, Pittsburgh, Pa.
J. Murray Weed, Schenectady, N. Y.
E. E. Wells, Montreal, Canada.
A. J. Westman, Montreal, Canada.
Mrs. A. W. Whitaker, Massena, N. Y.
G. S. Whitby, Montreal, Canada.
Walter B. Woodland, Montreal, Canada.
Mrs. W. B. Woodland, Montreal, Canada.
J. C. Woodson, East Pittsburgh, Pa.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 21, 1922, President Schlueder-berg in the Chair.

EFFECT OF HEAT TREATMENT ON THE HARDNESS AND MICRO-STRUCTURE OF ELECTROLYTICALLY DEPOSITED IRON.[1]

By Norman B. Pilling[2]

Abstract.

1. Some physical changes accompanying the heating of pure electrolytically-deposited (cathode) iron have been studied.

2. The initial effect of annealing is a very marked hardening, reaching a maximum at an annealing temperature of 300 - 400° C. The corresponding scleroscope hardness number is 45. At the same time the initial brittleness is removed.

3. Heating at higher temperatures results in progressive softening, consummated above the A_3 temperature (900°C.).

4. Microstructural changes and the rate of decomposition of the unstable iron-hydrogen compound are discussed in relation to the hardness changes.

In the past few years, considerable attention has been given in Great Britain and in this country to a means of salvaging valuable machine parts in which certain critical dimensions were undersize, due either to wear in service or to errors in manufacture, by the electrolytic deposition of a layer of iron upon the surface followed by machining back to size.[3] The present brief paper gives some results of an experimental effort to find in what way the properties of such electroplated iron are subject to modification by simple heat treatment.

The exact constitutional nature of electrolytically deposited iron has not been determined, but some general features regarding it

[1] Manuscript received August 4, 1922.

[2] Metallurgist, Research Laboratory, Westinghouse Elec. and Mfg. Co. East Pittsburgh, Pa.

[3] B. H. Thomas, Automotive Industries (Aug. 26, 1920). D. R. Kellogg, Electrolytic Deposition of Iron for Building up Worn or Undersized Parts. Trans. Am. Inst. Mining & Met. Engrs., 1922.

are well known.[4] The conditions of electrolysis, especially acidity and temperature of the electrolyte, have a remarkable effect upon the properties of the resultant deposit. In general, depositions made in hot solutions with the acidity kept low are soft and ductile, and have other characteristics similar to iron which has solidified from fusion, while cold and acid solutions yield a metal differing in many striking ways. It is hard, very brittle, showing a strong tendency to cleave in planes normal to the surface of deposition; its structure as revealed microscopically is totally different, consisting of closely packed needles, all roughly parallel and extending in the direction of growth; it can be softened by annealing and during annealing large quantities of gaseous hydrogen are released. The hydrogen is probably combined with, and not merely absorbed in the iron.

The material with which the following experiments were made was a quantity of iron of the latter type, twice refined electrolytically and stripped from the cathode in the form of sheets approximately 5 mm. thick. This iron was prepared by Mr. T. D. Yensen[5] under the conditions stated in Table I.

TABLE I.

Lot No.	S-4
Raw Material	Armco Iron
Electrolyte	$FeSO_4$, $7H_2O$; $FeCl_2$ $4H_2O$; $(NH_4)_2$ SO_4; $(NH_4)_2$ C_2O_4 H_2O
Temp. of Electrolyte	Room Temperature
Circulation of electrolyte	Yes
Current density	10 amp. per sq. dm.

Composition of Deposited Iron

Percent		Percent	
S	0.005	Mn	0.001
P	0.005	Si	0.022
C	0.005	Cu	Trace
		H	0.11

[4] For example, O. W. Storey: Microscopic Study of Electrodeposited Iron. Trans. Am. Electrochem. Soc. 1914, **25**, 201.
W. A. Macfayden: An Aspect of Electrolytic Iron Deposition. Trans. Faraday Soc. 1920, **25**, 98.
W. E. Hughes: Some Defects of Electro-Deposited Iron, Iron and Steel Inst. 1920, **101**, 321.

[5] T. D. Yensen: Preparation of Pure Alloys for Magnetic Purposes, Trans. Am. Electrochem. Soc. 1917, **32**, 165.

This iron was prepared to form a supply of pure iron for use in the production of pure ferrous alloys; consequently, certain of the conditions of electrolysis are not best suited for the deposition of a wholly homogeneous material. For example, the relatively high current density has produced a somewhat mammillary surface, resulting, as will be shown later, in a more variable internal crystalline arrangement, which in turn is reflected in the exhibition of a somewhat variable point-to-point hardness. Such minor differences will not detract from the significance of the observations, which are indicative of deep seated constitutional changes.

EXPERIMENTAL DETAILS.

The softening by annealing has been followed in some detail by annealing suitable samples at 100° intervals up to a maximum of 950°C. The heat treatments were carried out in a small electric tube furnace; temperatures were measured with a platinum-platinum rhodium couple lying adjacent to the specimen. No attempt was made to exclude air; in the low temperature anneals the oxidation was mainly a surface discoloration; in those at high temperatures, a thin scale of oxide formed. Subsequent examinations were made on surfaces well below the outside. The time of annealing was approximately 30 minutes; the time required to bring the specimen to the annealing temperature introduces an uncertainty of several minutes. The actual times are recorded in the tabular data and are sufficiently alike to permit comparisons.

HARDNESS.

The scleroscope hardness (universal hammer) of the annealed set of irons was measured. In view of the small mass of the specimens it was found necessary to take several precautions, especially with regard to parallelism between opposite surfaces. Plane parallel surfaces were ground with a surface grinder, and were later given a smoother finish on a metallographic belt grinder. Nevertheless, a considerable variation in hardness was noted, of which much was felt to be due to actual differential hardness in the material. This was especially evident in planes parallel to the surface of deposition. Measurements in perpendicular planes were found to be much more concordant, and principal stress will be laid upon them.

The hardness and other data are given in Table II. For the sake of comparison, to indicate the completeness of the softening by annealing, the hardness of a normal iron is given at the foot of the table. This sample was from an ingot of electrolytic iron which had been successively melted, forged, annealed, cold rolled to 20 percent reduction and annealed again at 940° C., leaving it in a fine grained condition.

TABLE II.

No.	Temp. of Anneal °C.	Time of Anneal Min.		Scleroscope Hardness			
				Perpendicular to Surface of Deposition		Parallel to Surface of Deposition	
		Pre-heat	An-neal	Average Hardness	No. Meas-urements	Inside	Outside
1876	30	...	...	26.2	18	25.5	23.0
3551	100	1	31	27.0	16		
1885	194	10	48	25.0	16	31.5	31.8
3552	200	9	30	26.4	17		
1884	300	7	32	45.3	12	39.4	33.7
1883	394	5	36	44.2	16	36.3	35.2
1882	512	5	30	36.6	13	32.1	28.8
1881	607	2	30	32.0	9	35.0	35.4
1880	696	5	30	25.6	20	26.8	21.7
1879	793	3	32	16.0	10	20.0	13.3
1878	900	2	30	23.5	11	23.1	22.3
1877	944	3	33	15.3	18	16.1	15.3
1429	*	...	...	17.3	17		

* Melted, forged, rolled, and annealed.

The hardness data taken perpendicular to the plane of deposition have been plotted, and are shown in Fig. 1. The original hardness of the deposited iron is retained unaffected by annealing up to 200°C. At 300°C. the primary effect is felt, and consists in a considerable additional hardening, an increase of over 70 percent being noted. Annealing at successively higher temperatures results in a progressive softening from a maximum between 300 and 400° C., and practically complete softening is obtained at 800°C. A slight increase in hardness follows immediately after the A_3 transformation at about 900° C.

The degree to which the hardness can be satisfactorily measured is indicated by the concordance between individual measurements. A typical case is that of the hardest specimen, of which the individual measurements were:

No. 1884 { 43.0 — 45.2 — 43.3 — 45.2 — 45.3 — 47.2 / 47.4 — 47.1 — 45.2 — 45.3 — 44.3 — 45.2 } Av. 45.3

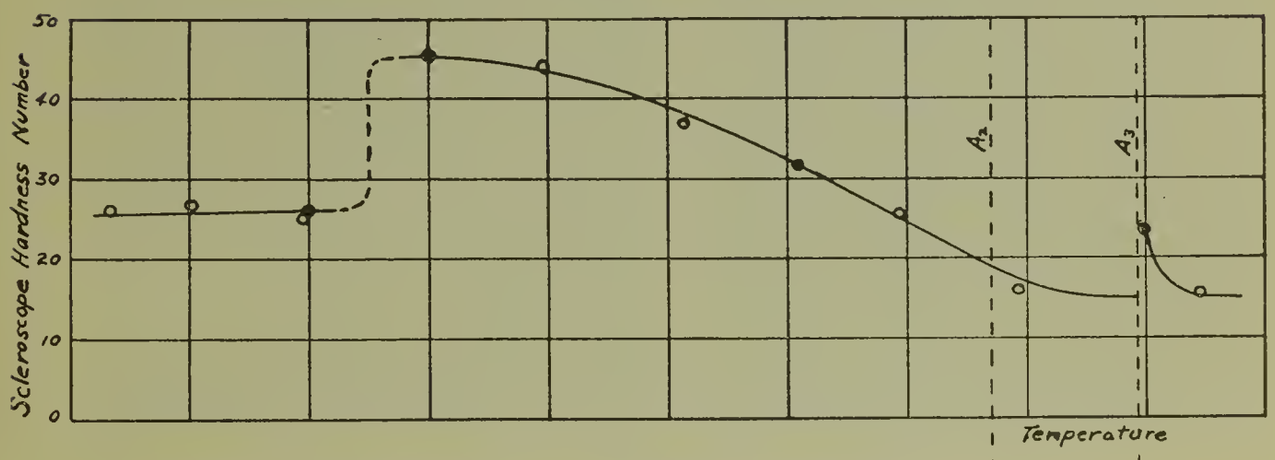


FIG. 1 HARDNESS OF ANNEALED ELECTROLYTICALLY DEPOSITED IRON

FIG. 2 SCHEMATIC REPRESENTATION OF STRUCTURAL CHANGES DURING ANNEALING

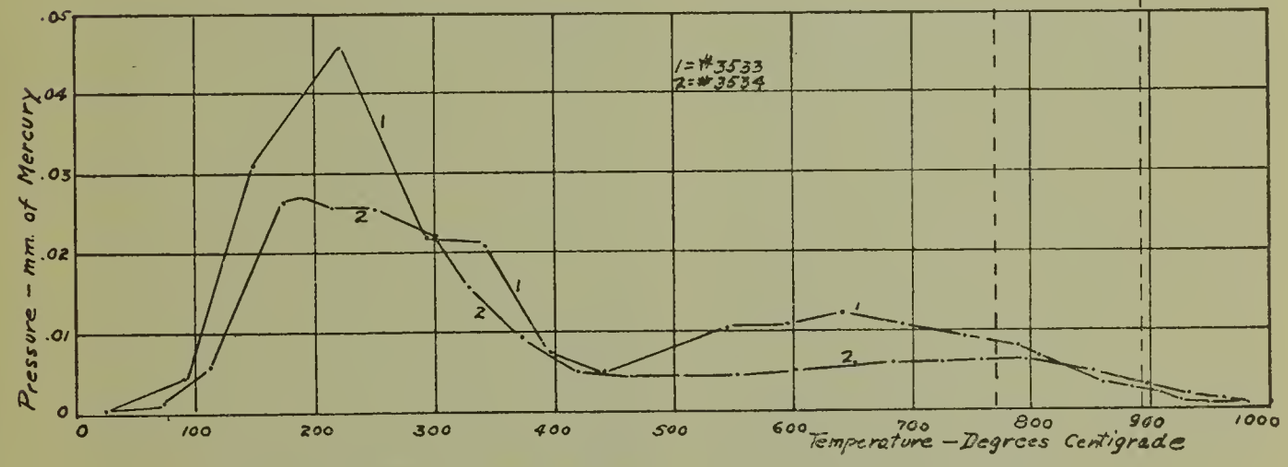


FIG. 3 RATE OF EVOLUTION OF HYDROGEN FROM E.D. IRON ON HEATING

The hardness measurements taken in planes at right angles, *i. e.*, parallel to the surface of deposition, are more irregular, but will be found to follow in a more or less sketchy way the curve which has been plotted. The hardness in these planes is quite generally lower than in the former.

The toughness also undergoes a change during annealing, although this is less easily demonstrated on account of the unfavorable shape of the material available. Fig. 16 is a photograph of

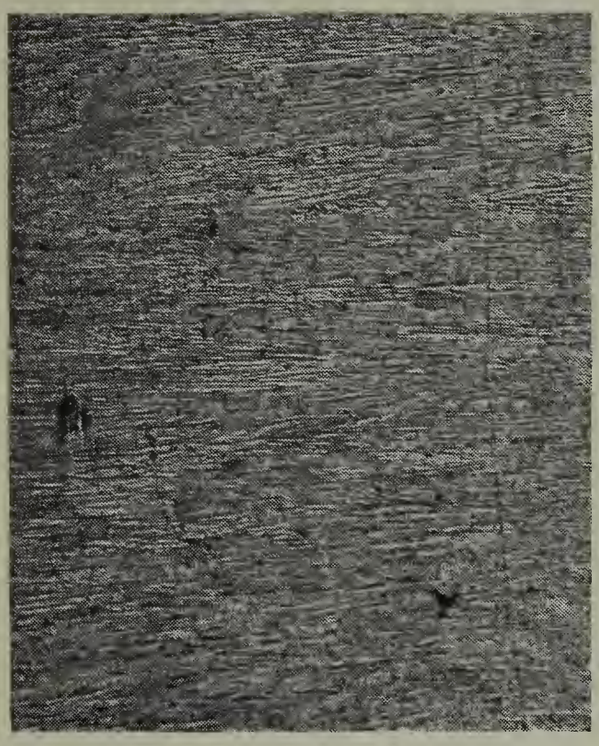
three samples, annealing temperatures 30°, 200° and 300°C. respectively, upon which an attempt was made to stencil the numeral 4. The 30° (raw) material shattered at the first hammer blow; the 200° one cracked into several pieces, while the 300° specimen resisted five blows of the hammer and deformed satisfactorily. All samples annealed above 300° C. could be stencilled. In this connection it may be said that even with extremely brittle pieces some deformation (cutting) preceded splitting, and for this reason the hardness measurements below 300° C. are considered valid. The scleroscope indentations were examined microscopically, and no indications of pulverization or local fissuring could be seen, which would be indicative of fictitiously low readings.

The extent to which electrolytically deposited iron can be hardened by a low temperature annealing deserves special remark. The scleroscope hardness 45, which is the maximum hardness developed, is equivalent to the hardness of a high carbon (1.2 percent C) steel in the annealed condition. The fact that the scleroscope measurements on this unusual type of material do indicate truly the nominal hardness in its generally accepted sense is shown by the following simple cutting test.

A bar of annealed 1 percent carbon steel, showing a scleroscope hardness of 33, was ground flat; a sharp corner of raw electrolytic iron would not cut it, but glazed the surface. A similar corner of hardened electrolytic iron cut this surface easily, and was in turn not cut by the steel.

MICROSTRUCTURAL CHANGES.

In Figs. 4 to 15 a series of micrographs are shown at 100 diameters, taken of a perpendicular plane. These illustrate the structural changes which occur during annealing. The cathode iron in the raw or unannealed condition (Fig. 4) is composed essentially of closely packed needle-like crystals, generally directed perpendicular to the surface of the cathode. In the case of deposits formed at relatively high rates the rate of deposition is not uniform over the surface, and at certain favored spots mammillary protuberances are formed. Within such protuberances the needle crystals are found to be arranged radially from a nucleus, as suggested by Fig. 5. This results in a varying angle

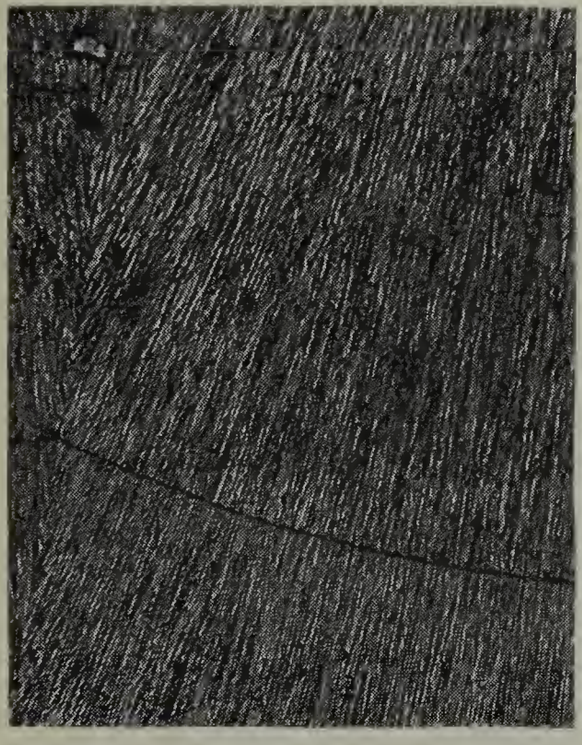


× 100

FIG. 4. Not annealed (1876-1)

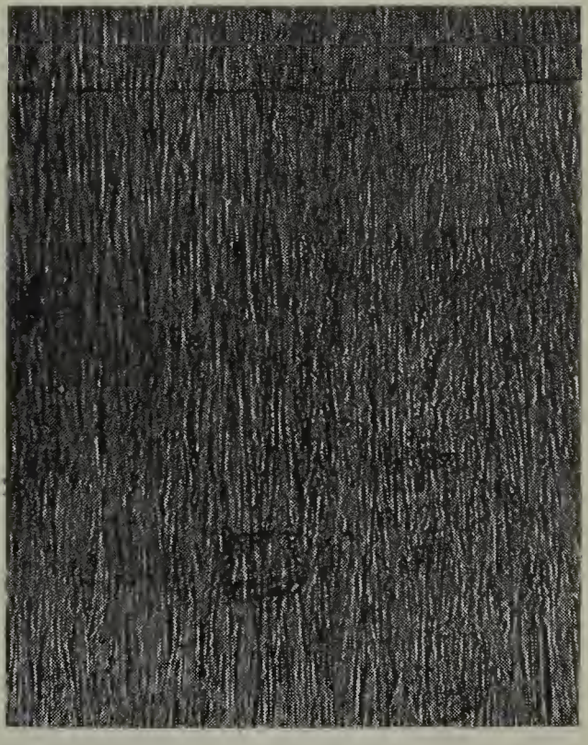
× 100

FIG. 5. Not annealed, oblique section (1822-1)



× 100

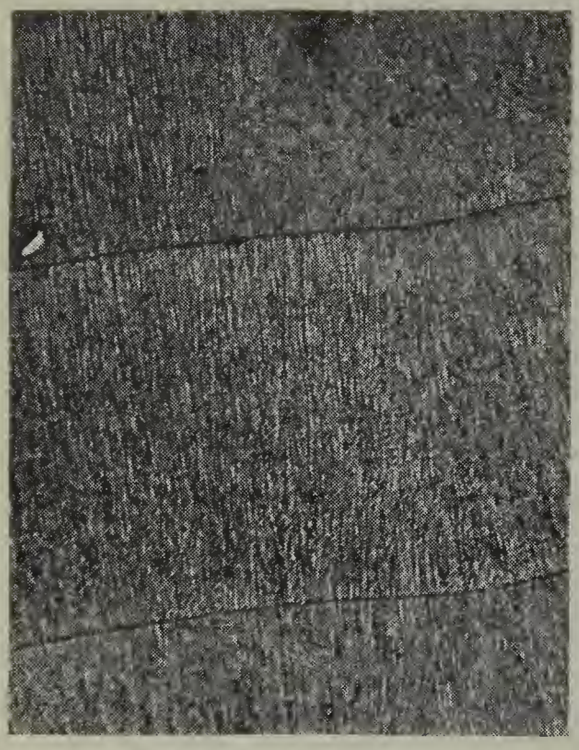
FIG. 6. Annealed at 101° C. (1886-1)



× 100

FIG. 7. Annealed at 194° C. (1885-1)

All etched with 10 percent solution nitric acid in ethyl alcohol.



× 100

FIG. 8. Annealed at 302° C. (1884-1)

× 100

FIG. 9. Annealed at 394° C. (1883-1)

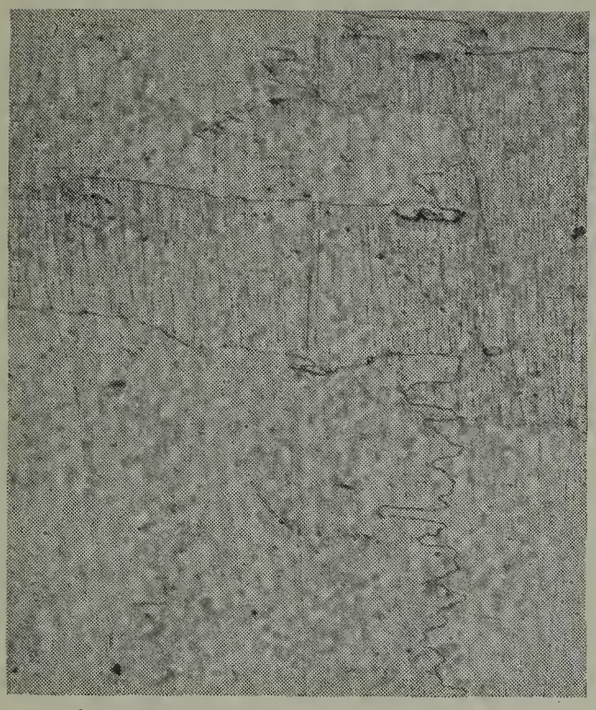
× 100

FIG. 10. Annealed at 512° C. (1882-2)

× 100

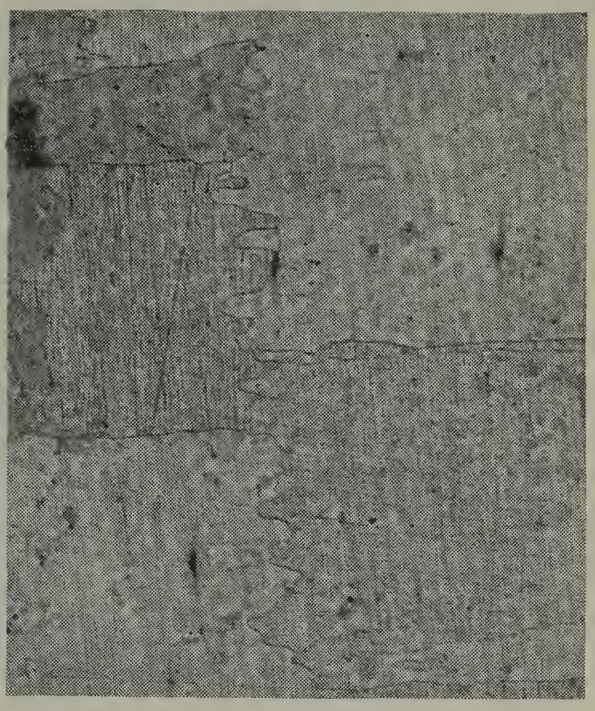
FIG. 11. Annealed at 607° C. (1881-3)

All etched with 10 percent solution nitric acid in ethyl alcohol.



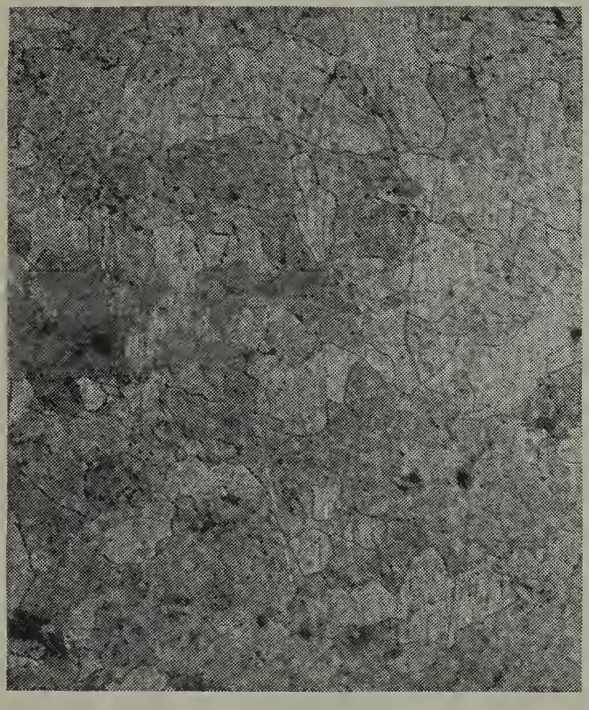
× 100

FIG. 12. Annealed at 696° C. (1880-2)



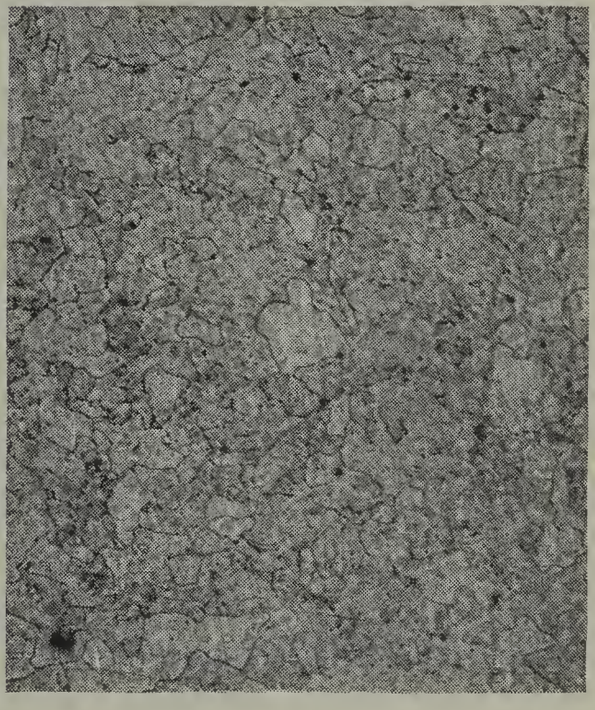
× 100

FIG. 13. Annealed at 793° C. (1879-2)



× 100

FIG. 14. Annealed at 900° C. (1878-2)



× 100

FIG. 15. Annealed at 944° C. (1877-2)

All etched with 10 percent solution nitric acid in ethyl alcohol.

of incidence in any plane and would lead one to expect point-to-point hardness variations. Temporary cessations in deposition leave their mark in the form of very thin oxidized surfaces or scars, parallel to the cathode surface and corresponding to the existing surface contour. It will be noted that upon the resumption of deposition this oxidized surface does not interfere with the crystalline orientation (Fig. 6).

The structural changes resulting from low temperature heating are on an exceedingly minute scale. At 300°C. (Fig. 8) a structural decomposition is evidently in progress, manifested by an indistinctness in definition of the needle crystals, but examina-

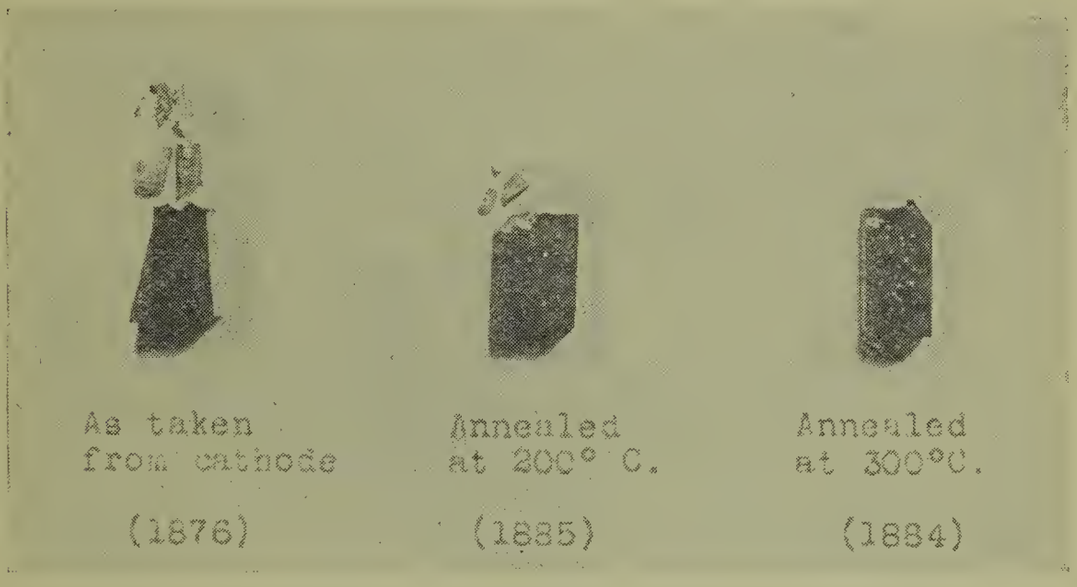


FIG. 16.
Increase in toughness of electrolytically deposited iron developed by annealing.

tion at high magnifications (1.8 mm. oil immersion objective) has not succeeded in giving more definite assurance of this. No further change other than the degree to which this is shown occurs until 600°C. when a distinct coalescence into large units of similar crystallographic orientation begins (Fig. 11). It will be noted that in these new crystals (the light area in Fig. 11) the needle-like striations are no longer present. At 700°C. (Fig. 12) the primary recrystallization is complete, and the iron is composed structurally of large elongated grains, their length quite generally perpendicular to the original surface of deposition.

It is interesting to note that the oxidized scars have been reduced by the liberated hydrogen, but not before acting effectively as a barrier to the amalgamation of crystals lying on either side, a

behavior quite different from that noted above during deposition. The ragged crystalline boundaries in Figs. 12 and 13 illustrate this. At 900°C. the well known A_3 transformation occurs, accompanied by a complete structural erasure. Annealings conducted at this temperature or above result in a very small, roughly polygonal-grain structure, from which all traces of the original structure have been removed, and resembling very closely iron which has initially been fused.

RATE OF DECOMPOSITION OF IRON-HYDROGEN COMPOUND.

The rate of decomposition of the unstable iron-hydrogen compound, which is assumed to be an essential component of this electro-iron, was observed at different temperatures. A fragment of cathode iron was taken, the rust cleaned off, dried at about 50° C. and pulverized. It was then placed in an alundum boat and slowly heated (average rate of heating 100 - 800° C. = 13° per minute) in a vacuum furnace, exhausted with a standard set of mercury diffusion pumps. It can be shown that the pressure in a container which is being exhausted at constant rate is a function of the rate of evolution of gas within it, both quantities increasing together, but not necessarily proportionally. Therefore, the pressure in the vacuum furnace is an indication of the rate at which gaseous hydrogen is being liberated due to the decomposition of the iron-hydrogen compound. Two curves determined in this way, agreeing in their general characteristics are shown in Fig. 3. The two plotted points indicated by arrows at 660° and 120° C. are the pressures registered during cooling, after the complete expulsion of hydrogen and with the rate of gaseous evolution then very low. From these curves the following points may be made.

1. The compound is actively decomposing at a temperature as low as 90° C.

2. The maximum rate of decomposition occurs at about 200° C.

3. Complete decomposition and expulsion of hydrogen is not achieved until the A_3 temperature is exceeded.

It would appear that the increase in rate of evolution above 500° C. is due to a slow release of hydrogen, by diffusion from the interior of the larger particles, rather than that a secondary reaction is taking place.

The quantity of hydrogen which is combined with the iron is at least indicated by the magnitude of the loss in weight by ignition *in vacuo*. This amounted to 0.11 percent in the case of the 13.5 gram sample from which curve No. 3533 was obtained.

CORRELATION OF OBSERVATIONS.

Figs. 1, 2 and 3, representing hardness change, structural change and gaseous evolution, have all been drawn to the same temperature scale to facilitate intercomparison. The sharp rise in hardness resulting from the anneal at 300° C. follows the maximum rate of decomposition (200°) and is accompanied by a visible microstructural alteration. Hence it may be inferred that this physical manifestation is the result of a constitutional change in the metal. Although unstable at 150° as shown by the copious gas release, this must be more or less in the nature of a surface action, for it is unaccompanied by an internal physical change, and not until a higher temperature is reached (300°) does the unbalance become sufficiently great for the decomposition to become general throughout the mass.

In its technologic aspects the results may be summarized:

1. For complete and rapid softening, annealing at a relatively high temperature (800-900° C.) is necessary.
2. By annealing at 300-400°C. the initial hardness may be considerably increased. With the present material the scleroscope hardness was increased from 26 to 45, the latter equivalent to the hardness of an annealed high carbon steel (1.2 percent C).
3. The brittleness of the material as deposited may be removed by annealing at 300-400° C.

DISCUSSION.

WILLIAM BLUM[1]: I should like to inquire whether in those tests on the evolution of gas, it was essentially hydrogen, or whether there was any evidence obtained of other gas in the iron?

NORMAN B. PILLING: The gas was not saved after it was pumped off, and, although it was probably largely hydrogen, we have no analyses of it. The oxidized surface was nicely reduced during this gas expulsion.

[1] Chemist, Bureau of Standards, Washington, D. C.

COLIN G. FINK[2]: There are no hydrocarbons that you have detected?

NORMAN B. PILLING: The analysis of the untreated iron shows a very small amount of carbon there, about 0.01 percent, I think, which would limit the amount of hydrocarbons possible.

HENRY HOWARD[3]: Do you find in a metal treated under the high vacuum that the hardness is decreased more quickly than when it is heated without a vacuum?

NORMAN B. PILLING: No, we have not found that at all. Annealing in a gaseous hydrogen atmosphere will even remove the combined hydrogen.

WILLIAM BLUM: The effects of hydrogen may be important in connection with electrodecomposition of other metals, such as nickel. We have an apparent anomaly here; certainly it is confusing to ascribe the hardness to hydrogen, and then to find that the iron becomes still harder by removing the hydrogen.

NORMAN B. PILLING: As to what really causes the increase in hardness, I cannot say, but I presume that it has something to do with the breakdown of this hypothetical hydride, if you wish to call it that, reducing the effective grain size enormously. A very great decrease in grain size is accompanied by increased hardness in all metals, as far as I know. It seems to be a general phenomenon. The microstructural changes that take place during this increase in hardness are on an extremely minute scale.

H. M. WILLIAMS[4]: I would like to ask if any carburizing experiments have been made.

NORMAN B. PILLING: I can not answer that directly, but Mr. Alley, who is associated in this work, is here and he may be able to answer that.

J. D. ALLEY[5]: The work we did was of a little different nature. We used a hot bath, 60° C., with a higher current density, and the iron deposited in that case was different from the iron that Mr. Pilling used in his experiments. We were working entirely in building up worn parts, and we found, in most cases, it was

[2] Consulting Electrometallurgist, New York City.
[3] Grasselli Chemical Co., Cleveland, Ohio.
[4] Research Engineer, General Motors Res. Corp., Dayton, Ohio.
[5] Research Laboratory, Westinghouse Elec. & Mfg. Co., E. Pittsburgh, Pa.

not necessary to carburize, but we did some of that work to see if it could be done, and we found it could. I think that answers the question.

COLIN G. FINK: I understand that considerable quantities of this electrolytic iron are used by the Western Electric Company. Do you know whether the initial hardness disappears with age? Have you found any record that this iron softens even at room temperature?

NORMAN B. PILLING: This particular iron that we used here was made about four years ago, and it apparently is as hard today as it was then. That is, in large chunks, not in powdered form.

COLIN G. FINK: So the iron-hydrogen is a fairly stable complex.

NORMAN B. PILLING: I think so. Dr. Blum understood that the iron becomes harder and more brittle when it is heated. That is not the case; it becomes harder and less brittle.

W. E. HUGHES[6] (*Communicated*): It is difficult to find in what respect Mr. Pilling's paper has added to present-day knowledge of the properties of electrolytic iron. He considers two matters; namely, (1) the annealing, and (2) the re-crystallization of that metal. In a cursory way, he has something to say of the microstructure of the metal as deposited.

First, as regards his annealing experiments. This part of his work is more than covered by that of J. Cournet[7]. His method is that which Cournet adopted, and his assumption of the existence of an iron-hydrogen alloy in electrolytic iron was also made by Cournet. Mr. Pilling tells us nothing that Cournet has not already told.

Second, as regards his re-crystallization experiments. Many others have long since observed and recorded all that Mr. Pilling has found—and more. I refer, especially, to that model of research published in 1913 by Professor Carpenter and Dr. Stead[8].

Third, Mr. Pilling's remarks concerning the structure of unheated deposited iron are apt to mislead. It is not accurate to say

[6] Electrometallurgist, Seaford, Sussex, England.

[7] *Compt. rend.*, 1920, **171**, 170 "Sur le recuit de fer electrolytique."

[8] Jour. Iron & Steel Inst., 1913, 88, 119.

that "In general, depositions made in hot solutions with the acidity kept low are soft and ductile." As a fact, acid in an iron-plating solution causes the deposit to be fibrous and hard, whether the solution be hot or cold. Further, there is no evidence at all that "hydrogen is probably combined with, and not merely absorbed in the iron." M. von Schwarz has lately definitely shown that, in the much more likely case of zinc, there is no similar alloy in solid, deposited metal[9]; though the presence of a hydride in zinc sponge has been considered possible by some authors[10].

Generally, Mr. Pilling's experimental methods are not unexceptional. The results of heating in air a sample of electrolytic iron containing as much hydrogen as does Mr. Pilling's is not likely to lead to useful information; nor, indeed, is the determination of hardness on surfaces that have been polished likely to do so, especially if the resulting amorphous film described by Beilby,[11] has not been completely removed.

NORMAN B. PILLING (*Communicated*): Two of Mr. Hughes' criticisms deserve attention: (1) The surface on which the hardness measurements described were made, were not polished as he assumes, but ground to the smoothness necessary for the scleroscope test. In any event, the thickness of Beilby's amorphous layer is so minute that serious doubt may be entertained as to whether it would affect the hardness measurement by any of our comparatively crude methods of testing, the micro-character of course excepted. (2) The constitutional changes which take place on heating hard electrolytic iron seem to be concerned with the dissolution of an unstable arrangement, depending principally upon the temperature and not upon extraneous atmosphere, as indicated by the fact that hydrogen expulsion and its concomitant softening occur indifferent to whether the heating be performed in vacuum, in air or in molecular hydrogen.

Mr. Hughes' other remarks are apparently based on a misunderstanding which a more attentive reading of the paper may perhaps correct.

[9] In work shortly to be published.
[10] Siemens & Halske, Ger. Pat. 66592; but see Mylius & Fromm, Ber. **27**, 630.
[11] Brit. Assoc. Rep., 1901, p. 604.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 21, 1922, President Schlueder-berg in the Chair.

THE PREPARATION AND THE MECHANICAL PROPERTIES OF VACUUM-FUSED ALLOYS OF ELECTROLYTIC IRON WITH CARBON AND MANGANESE.[1]

By Robert P. Neville and John R. Cain[2]

Abstract.

This paper describes the preparation and mechanical properties of an extensive series of very pure alloys of electrolytic iron, carbon, and manganese, whose compositions were so chosen as to bring out the specific effects on pure iron of additions of manganese, additions of carbon, and additions of carbon and manganese together in varying relative proportions. The maximum content each of carbon and manganese in each series is about 1.6 percent; the minimum, 0 percent, or pure iron.

Three-pound ingots of the alloys were made by melting electrolytic iron under vacuum in an electric furnace in a crucible of pure magnesia, to which the carbon and manganese were added after fusion of the iron. From these ingots tensile specimens were made and tested in the annealed state. The data were tabulated in the order of increasing carbon for comparison and interpretation of results. The effects of carbon are shown by grouping the specimens according to manganese contents and plotting curves for each group, with values from tests for ordinates and carbon contents for abscissas. The effects of manganese are shown in a similar manner by regrouping the specimens according to carbon contents.

I. INTRODUCTION.

While many of the specific effects of carbon and manganese on the properties of iron are well known, and the knowledge is

[1] Published by the permission of the Director of the Bureau of Standards of the U. S. Department of Commerce. Manuscript received August 16, 1922.

[2] Associate Chemist and Research Associate, respectively, Bureau of Standards, Washington, D. C.

being usefully employed in the processes of manufacture, there remains in spite of many investigations, much that is not thoroughly understood. Manganese is known to affect the properties of steel in at least three well recognized ways: (1) When present in sufficient amount it eliminates the red-shortness due to the presence of sulphur; (2) it deoxidizes, or helps deoxidize the steel, thereby eliminating the harmful effects of oxides and gases, which in some cases cause brittleness on forging or rolling; (3) it confers definite physical properties. Nevertheless, there still remains a lack of knowledge as to the amount of manganese needed for each function.

The investigation described in this paper was conducted with the expectation that by determining the specific effects, separately and combined, of carbon and manganese on the properties of pure iron, some of these questions could be answered. This necessitated the preparation and testing of extensive series of alloys of iron, carbon, and manganese, from which all extraneous elements of either gaseous or solid nature were as nearly as possible excluded. The present investigation is the first of a proposed series dealing with the preparation and properties of pure iron alloys. The investigation was begun by A. W. Owens, formerly associate chemist of the Bureau of Standards.

Only a brief description of the method followed and a discussion of the results will be given at this time since the detailed record of the work is being published as a scientific paper of the Bureau of Standards. Those desiring further details are referred to this publication, in which there is also included a review of previous investigations of a similar nature.

II. PREPARATION OF THE ALLOYS.

1. *Fusion in Vacuo.*

Since the purpose of the work was to study the specific effects on iron of carbon and manganese uninfluenced by other elements, it was necessary to exercise great care to have conditions such that other influences would be reduced to a minimum. This not only required that the impurities in the alloys be the lowest possible, but also that special consideration be given the method of fusion.

The influence of gases on the properties of metals is more and more being recognized as of great importance. Metals are known to contain relatively enormous volumes of gases either dissolved, occluded, or in chemical combination, which are known to greatly affect their properties. On this account, in order that these influences might be obviated, the melting of all alloys was conducted *in vacuo*.

2. *Materials Used.*

(*a*) *Iron.* The iron used in the preparation of the alloys was purified by the usual method of electro-deposition employed at the Bureau of Standards. This method has been described by Cain, Schramm, and Cleaves in the Bureau of Standards Scientific Papers[3]. It is essentially the deposition of iron from a 25 to 30 percent ferrous chloride solution on cathodes of ⅛-inch sheet "Armco" ingot iron. The electrolyte is prepared by dissolving "Armco" iron in 1:1 chemically pure hydrochloric acid. No addition is made to the electrolyte and the bath is operated at room temperature and without stirring. The current density is about 10 amperes per sq. dm. The iron deposits as a porous sheet which, if so desired, may usually be stripped from the cathode without breaking. Iron so deposited is very brittle, a feature which is undoubtedly the result of occluded hydrogen. This brittleness was, in the present instance, a decided advantage since for melting in the vacuum furnaces all the iron had to be crushed to small pieces in order to conserve space in charging the crucible.

Immediately on being stripped from the cathode the electrolytic iron received very careful cleaning, as it corrodes rapidly unless precautions are taken. If properly cleaned and dried the iron corrodes only slightly in air. Storing in sealed containers or in desiccators over calcium chloride is much more satisfactory. The cleaning was done by soaking the iron in dilute hydrochloric acid, in order to remove adhering basic salts. The acid was thoroughly removed by washing in distilled water. Drying was accomplished by two washings in alcohol followed by a final washing in ether. It was found that igniting the alcohol and allowing it quickly to burn away served as well as the washing with ether. The

[3] J. R. Cain, E. Schramm, and H. E. Cleaves, Preparation of Pure Iron and Iron-Carbon Alloys, Sci. Papers, No. 266.

iron was cleaned immediately on removal from the electrolytic bath (only a short time before using) and then stored in paraffin sealed bottles until used.

As deposited the iron normally contained the following percentages of impurities: C, 0.004; S, 0.004; Si, 0.001; Cu, Ni, and Co together, 0.014. When fused into ingots the impurities were slightly increased, with maximum values: C, 0.02; S, 0.008; Si, 0.008; Cu, Ni, and Co together, 0.014 percent. The carbon entering during fusion came from the graphite resistance heater of the electric furnace employed for melting the iron.

(*b*) *Manganese.* The most nearly pure manganese that could be obtained was used. It was by chemical analysis 98.75 percent manganese. The amount and nature of the impurities, nearly all iron with some carbon, made them of no consequence in the preparation of the desired alloys.

(*c*) *Carbon.* The carbon used was powdered Acheson graphite. It was not, however, added in this form. It was added as an iron-carbon alloy of 4.45 percent carbon. This alloy was prepared by melting electrolytic iron with an excess of graphite in a graphite lined crucible. A No. 20 plumbago crucible was lined with a half-inch coating of the powdered Acheson graphite moistened with a 1:1 solution of glucose in water. The lined crucible was then dried several hours in an oven at about 150° C. The charge, consisting of electrolytic iron with about 4.75 percent of its weight of powdered graphite, was placed in the crucible and melted in a gas-fired crucible furnace. The charge was kept molten long enough to insure thorough saturation and diffusion, after which it was allowed to cool with the furnace. Thus these melts contained the maximum amount of carbon which iron would dissolve under the conditions obtaining. This amount, 4.45 percent, was very nearly the same for the different lots prepared.

3. *Furnaces.*

The iron-carbon-manganese alloys were prepared in electric vacuum furnaces of the Arsem type, capable of attaining temperatures around 1,800° C. Vacuum melting was important in eliminating any possible influence of gases on the properties of the alloys. It also made possible the preparation of sound ingots of

pure iron and its alloys without adding, in the capacity of deoxidizers, any elements other than the carbon and manganese desired.

4. *Crucibles.*

The vacuum-fused alloys were melted in crucibles of pure magnesium oxide. No commercial source of refractory magnesia of sufficient purity was ever found. The greatest task of the whole investigation was the preparation of material for, and the making of crucibles which would not contaminate the pure molten iron. A comprehensive discussion of experiences with refractory crucibles for making these alloys would constitute a paper in itself.

Briefly described, the most practical method employed was as follows: U. S. P. magnesium carbonate was moistened with a water solution of glucose and pressed into briquets. These were dried and calcined at about 1,700° C. in a gas-fired furnace for several hours. This burning sintered and shrank the magnesium oxide enough so that, when ground to pass a 40-mesh sieve, the product was ready to make into crucibles. Crucibles were prepared by tamping the water moistened magnesia into a graphite mold around a wooden mandrel. The mandrel was removed and mold and crucible together dried and then calcined in the Arsem furnace at a temperature slightly above that at which it was to be used. This calcination caused the magnesia crucible to shrink away from the graphite. Since magnesia is so fragile at high temperatures, these crucibles were used in the graphite shells in which they were made. The space intervening between the walls of the graphite shell and the crucible was filled in with powdered graphite to support the magnesia under the pressure of the molten metal.

5. *Melting Procedure.*

The iron of the charge was placed in the crucible and melted. During the melting of the iron the carbon alloy and manganese were held suspended above the crucible in the cool portion of the furnace. After becoming thoroughly molten the iron was allowed to cool to incipient freezing, whereupon the alloying materials, suspended above, were dropped. This was done by passing an electric current through the small iron supporting wire

from which the charge was suspended. The instantaneous fusion of this wire allowed this additional portion of the charge to drop into the crucible on the barely molten iron.[4]

Invariably there was a strong ebullition when the carbon dissolved, which might become violent if care was not taken that the iron was at the proper temperature when the addition was made. This often caused results disastrous both to the melt itself and the helical heater of the furnace. After the carbon and manganese had been added the melt was held at a temperature of 50 to 100° C. above its melting point for about 30 minutes to insure thorough diffusion as no stirring was possible.

Unless the melt was carefully watched at this stage unfortunate results were liable to follow. If the temperature was allowed to go too high, strong agitation set in which, unless the temperature was instantly decreased, would often become so violent as to eject a large portion of the melt. If this happened, the graphite heater of the furnace was probably seriously damaged or the magnesia crucible was liable to break and allow the molten charge to run out into the furnace. Since the range between the minimum temperature for thorough diffusion and the temperature at which this agitation became violent was rather narrow, many melts were lost in this way. The temperature at which the agitation began was quite definite for each composition, being lowered as the carbon content increased. This agitation was advantageous in securing thorough mixing, but the difficulty in properly controlling it hindered its efficient utilization. This phenomenon, whether actual boiling or escaping of gases, was observed in melts of all compositions from pure iron to the alloys of the highest carbon and manganese content. It had many of the characteristics of a boiling point. It would repeatedly begin or stop at a definite point as the temperature increased or decreased.

6. *The Ingots.*

The melts were allowed to cool in the vacuum furnace and the ingots removed from the crucible by breaking away the magnesia. Their size was 1.8 inches in diameter at the top,

[4] This method was taken from Yensen and Gatward's paper, Magnetic and Other Properties of Iron-Aluminum Alloys Melted *in vacuo,* University of Illinois, Eng. Exp. Station Bull. No. 95, p. 11.

1.4 inches at the bottom, and about 8.3 inches long. They were all free from blowholes and sound, except that there was in the majority of them either a pipe with a small pinhole near the top opening into a larger cavity inside, or else a contracted area all around the ingot near the top like a neck. Whenever there was a "neck" there was never noticeable an interior pipe, and *vice versa*. A few ingots had neither this contracted "neck" area nor a pipe with an external opening. One of these was split longitudinally, and an internal pipe was found near the top, but not opening to the outside. Evidently there is always a certain amount of shrinkage on solidification, which may take place in any one of these three ways.

III. PREPARATION OF SPECIMENS FOR TESTING.

1. *Mechanical Work.*

The ingots were rolled hot. The starting temperature was 1,100° C. and the finishing temperature approximately 900° C. Since the ingots were small and cooled quickly, many heatings were necessary. The first passes were longitudinal, the reduction being 10 percent, until a length of 10 or 12 inches was reached, after which the remainder of the rolling was crosswise, with 7 percent reductions, to a minimum thickness of 0.5 inch. This made plates which after making end discards were approximately 9 inches long and 2 inches wide.

Bars 0.75 by 0.5 by 6 inches, from which the test specimens were to be turned, were cut from these plates. Two bars were cut from each plate, in order that there might be a check on each composition. These bars were turned down to tensile test specimens with reduced sections 2 inches in length and 0.38 inch in diameter. The ends were threaded. After heat treating, as described below, the specimens were ground down along the entire length of the reduced section to a diameter of 0.357 inch.

2. *Heat Treatment.*

It was considered advisable to subject all samples to a preliminary annealing in order to compensate for possible ingotism. Accordingly, the test bars were divided into three groups, according to the carbon content, irrespective of the manganese con-

tent. The first group contained those with carbon percentages from 0.0 to 0.09; the second group, 0.10 to 0.29; the third group, 0.30 to 1.60. The bars were heated in a mixture of magnesite and a small amount of charcoal to a temperature of 940° C. for the first group, 900° C. for the second, and 840° C. for the third; held at these respective temperatures for two hours and then cooled in the furnace to below 500° C.

After this preliminary treatment the bars were divided into small groups according to composition. The specimens of each group were then heated in an electric muffle furnace containing burning charcoal to a temperature corresponding to approximately 30° C. above the Ac_3 for that group, held at that temperature for 20 minutes, removed from the furnace, and cooled in still air.

IV. PROPERTIES OF THE ALLOYS.

1. *Mechanical Tests.*

The tension tests were made on an Amsler hydraulic testing machine. The usual standard methods were followed. Data for stress-strain curves were taken by means of a Ewing strain gauge.

After the tension tests had been made Brinell hardness determinations were made on the ends of the broken specimens. Since the specimens were of the round, threaded-end type, the ends had to be ground down before the impressions were made. Their surfaces were slightly polished and three impressions, using a 10 mm. ball and 3,000 kg. load, were made on each piece.

2. *Micro-examination.*

Each specimen was examined under the microscope, to detect any discrepancy in heat treatment or irregularity of structure. In order that the surface examined might be as near the fracture as possible and yet not in the strained portion of the test bar, one part of each broken test bar was sawed in two at the shoulder and photomicrographs made of this cross section. These photomicrographs furnish enough material in themselves to justify their consideration as a separate phase of the general study of the properties of these alloys.

3. *Mechanical Properties of Pure Iron.*

Since there have been so many estimations of the mechanical properties of very pure iron, and so few actual determinations, the data from the pure iron specimens of the series are of especial interest. The ultimate strengths of the two specimens were 41,700 and 42,200 lb./sq. in. The elongations in 2 inches were 40 and 41 percent, the reductions of area 80 and 85 percent (0.357 inch specimen), and the Brinell hardness numbers 69 and 70. These specimens were electrolytic, vacuum-fused iron, of about 99.98 percent purity.

4. *Chemical Analysis.*

The samples for chemical analysis were millings from the fractured ends of the specimens. Carbon, manganese, sulphur, and silicon were determined on every specimen. Analysis of every specimen for other elements seemed entirely unnecessary since the materials from which the alloys were prepared were the same throughout the series, and there was practically no chance for contamination by any element other than silicon and sulphur. A number of the specimens were analyzed for phosphorus, but it was never found in determinable quantities. Since the anodes used in the electrolytic purification contained small amounts of copper, cobalt, and nickel, analyses for these were made on some of the samples.

5. *Data.*

The plan according to which the alloys were made really consisted in the preparation of six different series. The first was a series of iron-carbon alloys whose carbon contents increased by steps of 0.1 from 0 to 1.60 percent. Five other series were made with these same carbon increments, the same in every respect as the first except that to each of them manganese had been added. They contained respectively 0.20, 0.40, 0.80, 1.20 and 1.40 percent manganese.

Such a plan should clearly show the manner in which carbon and manganese influence the properties of iron. A comparison of the properties of the iron-carbon alloys with those of pure iron should bring out the effects of carbon. Likewise, a com-

parison of the properties of the iron-manganese alloys with those of pure iron should bring out the effects of manganese. And so on with the iron-carbon-manganese alloys.

The nicety of the plan comes in the assurance that any differences in properties that may be observed in the alloys is due to differences in carbon or manganese content, as the case may be, and not due to the presence of extraneous elements. Impurities were of negligible amounts. Phosphorus was not present in any of the alloys. There was no manganese in the iron-carbon alloys. Sulphur and silicon were present in only such small quantities as 0.003 to 0.009 percent each. These amounts are so small as to be entirely negligible.

The mechanical tests consisted of determinations of ultimate strength, proportional limit, yield point, elongation, reduction of area, and Brinell hardness numbers. The yield points as a whole, however, were not entirely satisfactory. For alloys of lower carbon contents they were easily detected and very marked, but as the carbon contents began to become high they became less easy to detect. Stress-strain curves for the high carbon alloys had gradual slopes with no discernible breaks up to points of rupture.

V. INTERPRETATION OF DATA.

1.- *Effects of Carbon.*

In order to determine the influence of carbon on the properties of the alloys the data were tabulated by groups, each group comprised of specimens of approximately the same manganese content.

Data for the alloys by groups, the alloys of each group of approximately the same manganese content, were tabulated and compared. Curves were constructed for each of the properties. Test data were plotted against content. As the carbon contents increased ultimate strengths were raised in direct proportion, until the carbon was around 0.70 percent. From here on the proportionate increase became less. As the carbon increased beyond 0.90 or 1 percent the ultimate strength values decreased. Maximum ultimate strengths were always at carbon contents a little less than 1 percent.

The curves showing the effect of carbon on ultimate strength for ranges of manganese assembled on one graph are shown in Fig. 1. Curves for Brinell hardness numbers are almost identical with those for ultimate strengths. The two curves were practically parallel in each of the 6 series. Although to a

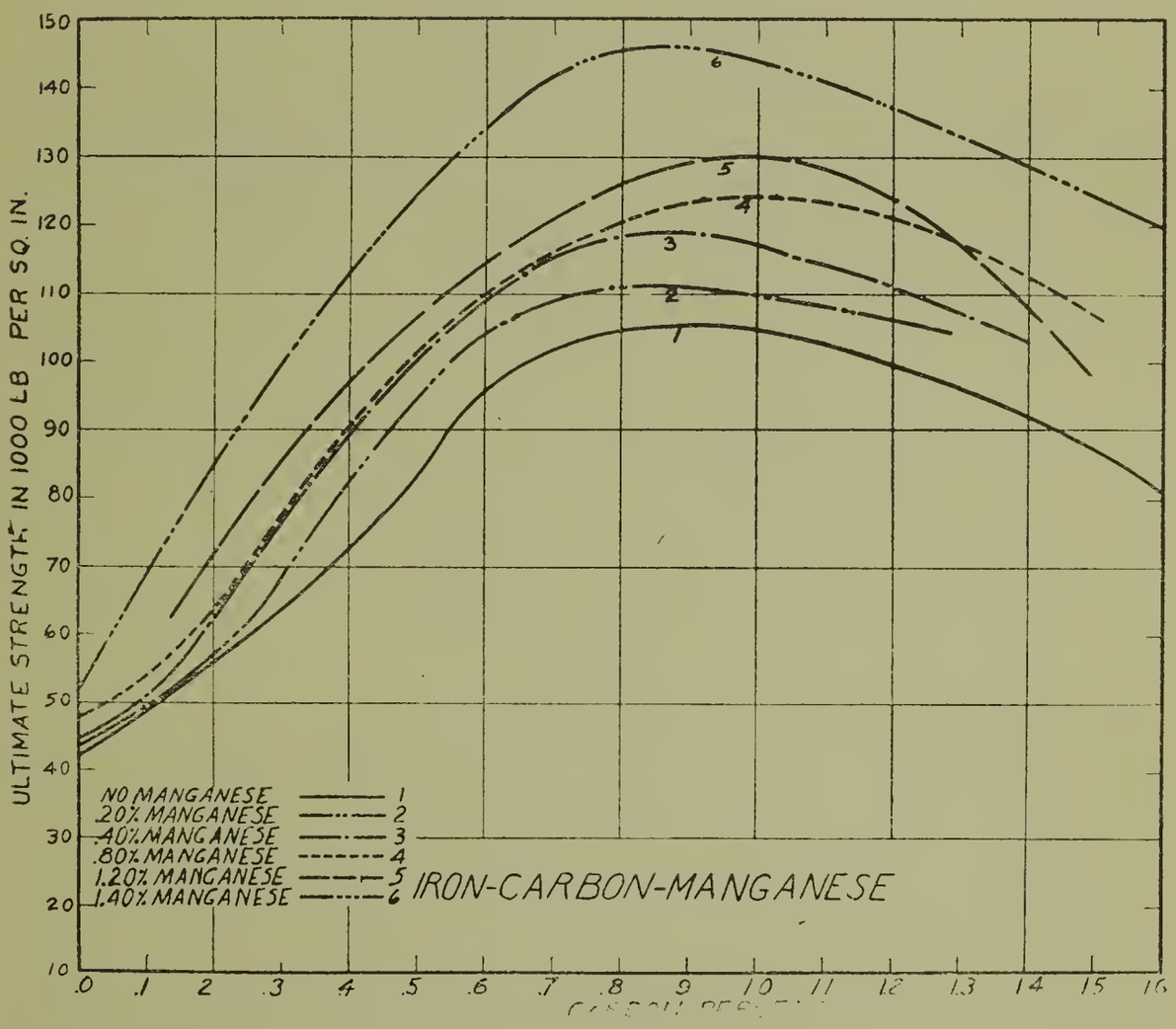


FIG. 1. Ultimate strength values plotted against carbon contents. The curves show the influence of carbon on the ultimate strength of alloys with different manganese contents.

lesser degree than the Brinell hardness numbers, the proportional limit curves are also similar to those for ultimate strength. Their slopes are less steep in ascent as the eutectoid composition is approached, break less suddenly, and slope down more gradually. Yield point curves are similar to those for porportional limits.

From a carbon content of 0 percent to contents around 0.90 or 1.00 percent, the values for the reduction of area were reduced from about 85 percent to about 5 or 10 percent. Increase in car-

bon above 1 percent decreased reduction of area very little more. Elongation for 0 percent carbon contents was about 40 percent. It is affected by increases in carbon, in about the same manner as is the reduction of area. The respective curves of each of the series are similar. There were some differences, accounted for by manganese, which will be discussed below.

2. *Effects of Manganese.*

Manganese in the absence of carbon seemed to have a very slight effect on the properties of iron. Ultimate strength, proportional limit, yield point, and hardness were slightly increased, but there appeared to be no relation between manganese content and either reduction of area or elongation. It thus appears that manganese has no influence on these two properties whether carbon is present or not. Manganese in the presence of carbon affected elongation and reduction of area not at all. Manganese does affect ultimate strength, Brinell hardness, and proportional limit, but not nearly as much as carbon. The effect on each property was about the same. The influence of manganese on the mechanical properties was greater when the carbon content was higher.

Fig. 2 shows graphically the influence of manganese on the ultimate strengths of the alloys. As with carbon, ultimate strength is plotted against composition—manganese in this case. In plotting these there were an insufficient number of alloys with exactly the same carbon content to construct reliable curves. Therefore, the alloys were placed in 6 groups, each group having a certain range of carbon. The influence of carbon is so much greater than that of manganese, that this lesser influence of manganese would be completely obscured by very small differences of carbon content. Accordingly, before plotting allowances were made for these differences in carbon. Like the ultimate strength curves. the curves for the other properties were straight lines. All are practically parallel with the exception of the two ductility curves which are horizontal.

3. *Combined Effects.*

Both carbon and manganese have more influence on the mechanical properties of iron according to the amount of the other

element present. Manganese in the absence of carbon affects the properties of iron very little. As soon as carbon is added this influence becomes more marked. Likewise, the same variation in the carbon content of an alloy of low or no manganese and one of higher manganese does not produce the same effect. The same difference in carbon has more effect when manganese is

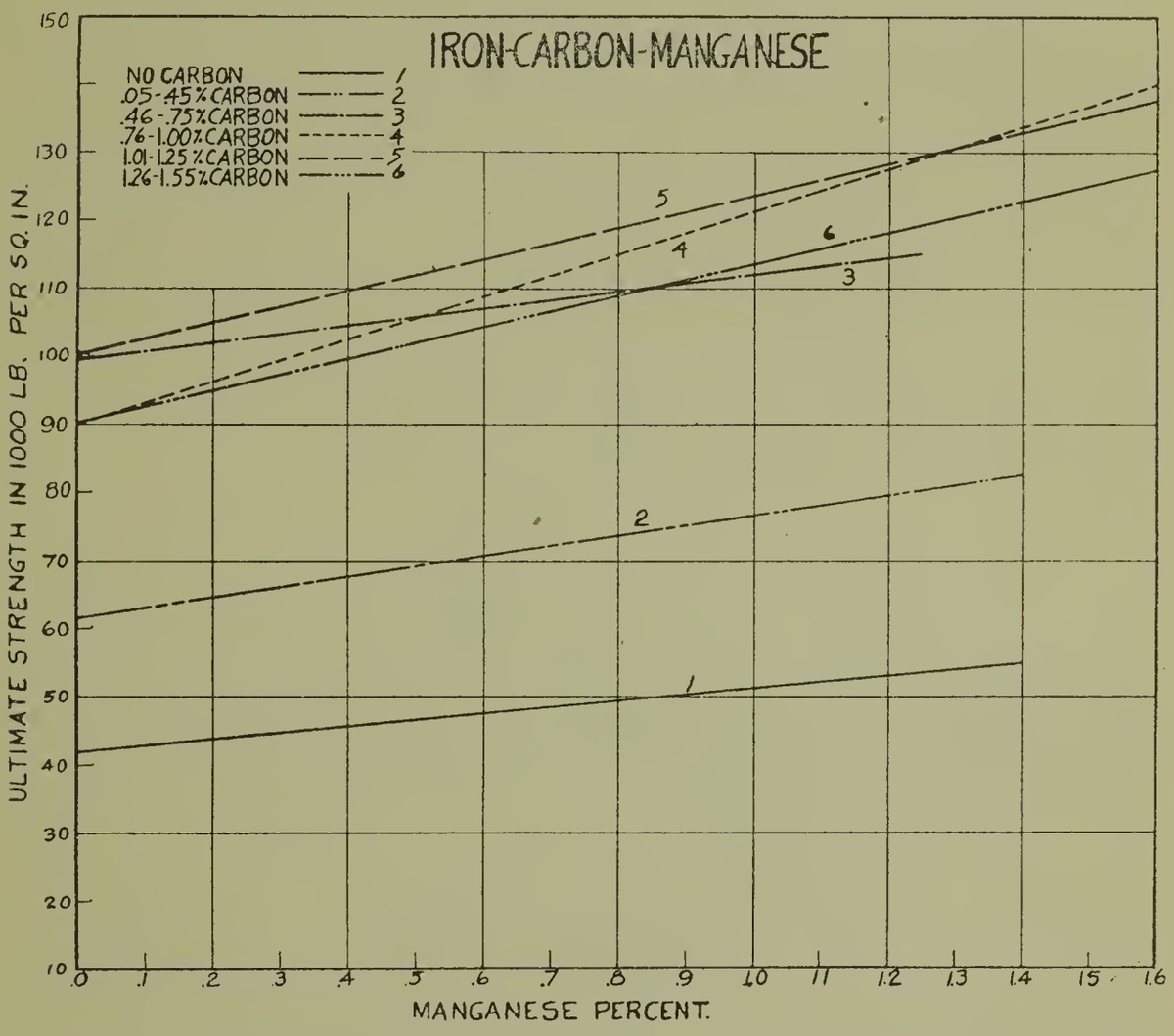


FIG. 2. Ultimate strength values plotted against manganese contents. The curves show the influence of manganese on the ultimate strength of alloys with different carbon contents.

present than when the alloy contains no manganese. The influence of carbon is increased accordingly as the manganese content becomes greater. Each influences the effect of the other.

A comparison of the effects of manganese on steels as reported by investigations of the influence of its constituents, with its effects on pure alloys fused *in vacuo,* is of particular interest. In some steels, especially those prepared by the Bessemer process,

the first additions of manganese cause a decrease in tensile properties as the manganese content increases, until its content amounts to about 0.35 percent, after which further increase has a strengthening effect. In these pure vacuum-fused alloys the effect of manganese was continuously positive from the lowest to the highest contents.

This seems in accordance with the theory that with steels the first additions of manganese serve to deoxidize the steel, forming oxides which tend to separate the grains, thereby decreasing its strength. Any excess of manganese then added over the amount required for deoxidation forms combinations beneficial to tensile properties. In the case of these alloys, or "pseudo" steels, absence of oxygen prevents the formation of weakening oxides when the first manganese is added. Accordingly, the first additions of manganese are available immediately to combine in a manner beneficial to the mechanical properties.

VII. SUMMARY.

1. Over a hundred alloys with negligible amounts of impurities were prepared from electrolytically purified iron, carbon, and manganese of very high purity by fusion *in vacuo* in crucibles of magnesia prepared especially for the purpose to prevent contamination during melting. The compositions were so chosen as to bring out the effects on pure iron of additions of small amounts of carbon, additions of small amounts of manganese, and additions of carbon and manganese together. The ranges in chemical composition of the alloys were from 0 to 1.6 percent carbon and 0 to 1.6 percent manganese. Ingots of about 3 pounds each were made and rolled to 0.5 inch plates, from which specimens for testing were cut. Ultimate strength, proportional limit, yield point, elongation, reduction of area, and Brinell hardness determinations, were made and photomicrographs taken.

2. In amounts below approximately 1 percent the ultimate strengths of the alloys were increased by carbon. The ratio of this strengthening effect to carbon content was not constant, but was within the limits of 875 and 1,150 lb./sq. in. for each 0.01 percent carbon between the limits of 0 and 0.70 percent. This strengthening effect was greater in the alloys of higher manganese

contents. An approximate average of the rate was 1,000 lb./sq. in. for each 0.01 percent carbon.

3. The hardness of the alloys was influenced by carbon in about the same manner as was the ultimate strength. The increase in hardness due to carbon was from 1.8 to 2.6 Brinell numbers for each 0.01 percent carbon, the rate being larger as the manganese contents increased.

4. Reduction of area and elongation of pure iron were 82.5 and 40.5 percent, respectively. With the addition of carbon these values were rapidly and regularly decreased with the increase in carbon, until values little greater than zero were reached around 1 percent. Increase in carbon beyond this point had little effect on ductility. These minimum values were reached at lower carbon contents when the manganese was increased.

5. Carbon influenced the proportional limits of the alloys less than the other properties. Although the effect on proportional limits was less easily discernible, it could be seen that the maximum values were reached at lower carbon contents than the maximum values for ultimate strengths, and remained at this maximum value over a wider range of carbon contents.

6. Manganese increased the ultimate strengths of the alloys only slightly, particularly with small amounts of carbon present. Expressed quantitatively, this rate of increase was about 90 to 250 lb./sq. in. for each 0.01 percent manganese.

7. Manganese influenced the proportional limits in about the same manner it did the ultimate strengths.

8. Brinell hardness numbers were increased about 0.5 by each 0.01 percent manganese when carbon was present. This rate was lower in the alloys of lower carbon contents.

9. Manganese had very little effect on the ductility of the alloys.

10. The effects of manganese and carbon on the mechanical properties of the alloys were each influenced by the other. The presence of carbon augmented the influence of manganese and *vice versa.*

Several acknowledgments should be made. In the preparation of this paper and throughout the entire investigation the sugges-

tions and advice of Louis Jordan, chemist, have been invaluable; the rolling of the ingots was done by R. G. Waltenberg and A. T. Derry, associate physicists; H. J. French, physicist, was responsible for the heat treatment; J. R. Freeman, Jr., associate physicist, assisted in the tension tests; microscopic examinations were made by H. S. Rawdon, physicist; H. A. Bright and W. G. Fedde, associate and assistant chemists, respectively, collaborated in carbon determinations.

DISCUSSION.

CARL HERING[1]: Reference has been made several times to the fact that there is carbon in electrolytic iron. It would be interesting to know how it got there. I suggested some years ago before this Society that it may get there by a mechanical migration from the anode; as the iron is dissolved, the carbon is mechanically set free and wanders over to the cathode and is there cemented on, so to speak, by the deposit. This is a mere suggestion.

WILLIAM BLUM[2]: Several years ago there was quite a controversy in the literature as to whether iron deposited from oxalate solutions in electroanalysis contains carbon. It was certainly proven that from solutions containing tartrate or citrate, carbon is present in the deposited iron, and there were indications that, even in oxalate solutions, traces of carbon may be carried over and deposited in the cathode iron.

With sulphate or chloride solutions, there would be no chance for carbon to be derived from the electrolyte itself and therefore the only possibility would be that suggested by Dr. Hering, that carbon either as such or in the form of hydrocarbons, which might be present in the original iron, is carried over mechanically into the deposit.

CARL HERING: Then it could be stopped by a filter, if not in solution.

WILLIAM BLUM: If the carbon is in colloidal solution in the electrolyte, the possibility of filtration will depend upon how fine the particles are.

[1] Consulting Electrical Engineer, Philadelphia, Pa.
[2] Chemist, Bureau of Standards, Washington, D. C.

COLIN G. FINK[3]: In support of the theory that Dr. Hering advanced, that the carbon is actually occluded or deposited mechanically, you need only to refer to the occlusion or the mechanical deposition of glue and other similar addition agents in the electrolytic refining of metals. As far as filtration goes, I do not think you will find a commercial filter which will stop these fine colloidal particles of carbon.

N. B. PILLING[4]: In regard to the possible uses for electrolytic iron, I understand that magnetically the very pure irons are very attractive.

R. P. NEVILLE (*Communicated*): In the course of previous investigations, experiments with filters were tried in an attempt to prevent any transportation of foreign particles from the anode to the cathode where they might be mechanically included in the iron deposit. When the anodes were enclosed in porous clay cups the quality of the deposit was not improved, except possibly there was a little more copper in the iron deposit when the cups were not used. This difference was so slight that the practice of using filters was not adopted.

[3] Consulting Electrometallurgist, New York City.
[4] Metallurgist, Research Lab., Westinghouse Elec. and Mfg. Co., E. Pittsburgh, Pa.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 21, 1922, President Schlueder-berg in the Chair.

THE DEZINCIFICATION OF BRASS.[1]

By Ralph B. Abrams[2]

Abstract.

Experiments are recorded, the results of which indicate that the mechanism of dezincification appears to be as follows: The first step is the dissolving of the brass as a whole. The copper in solution then redeposits replacing brass as a unit. This redeposition will not take place unless there is some means of holding the dissolved copper in contact with the brass. This can be accomplished in two ways, one by the presence of a membrane, the other by having a large excess of dissolved copper present. Obviously this latter possibility is a remote one, especially so far as natural conditions are concerned. The membrane may be anything whatsoever, so long as it performs the function of keeping the dissolved copper in contact with the brass. Whether or not dezincification shall take place can be controlled by merely supplying or taking away the membrane. Briefly then, the dezincification of brass is the dissolving of the brass as a whole, the holding of the dissolved copper in contact with the brass by a membrane, and the subsequent redeposition of the copper.

The subject of the dezincification of brass has been one of current interest for many years to students of the corrosion of non-ferrous alloys. This corrosion has been studied from almost every conceivable point of view, in an effort to throw light on its actual mechanism. Dezincified brass is commonly understood to mean brass which, after undergoing service for a period of years, has so disintegrated under the influence of sea water that only a

[1] Manuscript received July 7, 1922.

[2] Senior in Chemical Eng. Univ. of Wisconsin.

porous mass of seemingly metallic copper with a brass colored coating on the surface remains. It is really brass minus the zinc, and minus those physical qualities which make brass valuable. This product of corrosion is weak, brittle, and fails under the slightest stress.

In using the word "dezincification" in this paper, it is to be understood to mean brass which has undergone the corrosion above described, regardless of what the actual process of this corrosion has been. The question of dezincification has been one of vital import to users of brass condenser tubes and other brass parts which are subject to the action of sea water. It was perhaps the distress of the maritime users of brass that spurred the efforts of men of science to find the real cause of this action. As has been said, the question has been attacked from all sides. It may prove interesting to review a few of the more prominent ideas advanced. Mr. Arnold Philip, admiralty chemist, Portsmouth,[3] believes in the existence of "minute zinc-copper couples, functioning as small electrical cells, all over the surface of the brass." He called attention not only to molecular couples of copper and zinc, but also to molecular couples of compounds of copper and zinc. The action of such couples results, he believes, in the dissolving out of zinc and leaving copper behind.

Mr. Samuel Whyte and Dr. Desch concur in the idea of a couple action between the *alpha* and *beta* constituents of brass. Their idea agrees well with the statement by Mr. Rawdon.[4]

"The preferential attack of the *beta* phase is to be attributed to its higher zinc content, which renders it more electro-positive than the copper-rich *alpha* constituent. When an electrolyte is present, electrolysis occurs either by means of the application of an external e. m. f., by contact with some metal that is less electro-positive than the alloy, or by reason of the electrochemical difference in potential between the *alpha* and *beta* phases. The *beta* is always attacked first; its zinc largely passes into solution leaving behind the porous copper masses occupying the spaces initially filled with the *beta* matrix. This type of corrosion may be regarded as electrolytic leaching out of zinc."

[3] Journal of the Faraday Society, 1915, p. 244.

[4] Tech. Paper No. 103. Bureau of Standards.

A different opinion is presented by Dr. Bengough and Dr. Hudson in the fourth report of the British Corrosion Committee of the Institute of Metals.

"The provisional view of the present authors as regards 70:30 brass is that the normal action in ordinary types of neutral or nearly neutral water is predominantly one of oxidation, and that the action of couples if such exist is too seriously hampered to be effective.. . . . . .It does not appear to the authors a b s o l u t e l y c e r t a i n , however, that any copper is left *in situ* when zinc passes into solution; what a p p e a r s to be left may really be redeposited."

An extract[5] of the fifth report by the same committee was published a few months ago. In this, from a study of the corrosion of copper, it is concluded as follows:

"Also that the first action of the corrosion is upon a thin oxidized coating rather than upon the underlying metal. Now if a piece of smooth copper be immersed in chloride solutions, the oxidized surface gradually changes into an almost insoluble cuprous chloride (CuCl), which is ordinarily swept away by gravity or by water currents, but which may adhere to the surface. In the latter case cuprous chloride becomes oxidized according to the reaction

$$4CuCl + O = Cu_2O + 2CuCl_2$$

into cuprite crystals and the very corrosive soluble cupric chloride. It is easily proved that cupric chloride is very corrosive to copper

$$CuCl_2 + Cu = 2CuCl$$

and the end product is where we started from. Therefore the reactions occur in cycles at spots underneath the gelatinous salts permeable to oxygen in solution.

"Brass in chloride solution acts similarly. As noted before, the first attack gives a layer of copper oxide, plus a little zinc oxide, the zinc mainly going into solution as $ZnCl_2$. The reactions on the copper then proceed as outlined just above. If the insoluble chlorides adhere to the surface, cupric chloride is formed. Cupric chloride attacks zinc as well as copper,

$$CuCl_2 + Zn = ZnCl_2 + Cu$$

[5] Chem. and Met. Eng. Feb. 15, 1922. p. 305.

with the formation of a soluble zinc chloride and the deposition of crystalline or powdery copper."

It was in view of this diversity of opinion and because of the widespread interest in the problem that the present investigation was undertaken.

The great difficulty in attempting to study the actual mechanism of the so-called dezincification of brass is that under natural conditions the process requires several years. In the short time available for these experiments, it was therefore impossible to reproduce this corrosion by the mere immersion of brass in artificial sea water. Hence the problem was to hasten the action without distorting the results. Dilute hydrochloric acid presented itself as a probable agent to accomplish this. Corrosion by hydrochloric acid ought to be the same as corrosion by sodium chloride except that the discharge potential of hydrogen on brass from a hydrochloric acid solution is far below what it is from a sodium chloride solution. Therefore the action with hydrochloric acid should proceed with greater velocity than with sodium chloride. If this be the only difference in the performance of the two solutions, then the substitution of hydrochloric acid for sodium chloride should not affect the process of dezincification no matter what its mechanism is. This was tested by experiment. It will be well to mention here that the brass strips used in all the following experiments were about one millimeter in thickness, weighed 0.35 gram per square centimeter of area, and had a total weight of about 10 grams.

Experiment 1

Five brass strips were submerged in separate tumblers of normal hydrochloric acid and covered with glass plates to prevent evaporation. After four weeks the specimens were examined.

Result: In every case when the sample was removed from the hydrochloric acid, the acid not only showed no trace of the characteristic blue color of a copper salt in solution, but it was perfectly clear and colorless. The brass itself showed no sign of corrosion on the surface, except for the appearance of a few small particles of crystalline copper. The specimens were brittle and could be broken by the fingers with ease. Beneath a brass colored

surface the specimens were found to consist entirely of copper. In those cases where the corrosion had not gone to completion, there was a layer of brass at the center with layers of copper on either side. In two samples where the corrosion had gone completely through the thickness of the brass, instead of finding one continuous mass of copper, there were two distinct layers of copper which could easily be pulled apart. The surface between them was smooth and flat.

From the above result, the effect of dilute hydrochloric acid in producing dezincification can not be doubted. With this agent at hand with which the problem can be attacked, a systematic study of it can now be attempted. The first question is to show whether this phenomenon is a leaching out of the zinc or whether it must be explained by another theory.

Experiment 2.

Brass strips were submerged in normal hydrochloric acid. The solution was agitated by bubbling air through it.

Result: At the end of 26 hours the samples were completely dissolved. This experiment was repeated four times with the same result.

Experiment 3.

Brass strips were again placed in normal hydrochloric acid. This time a mechanical stirrer was used to keep the acid in motion. In this case no air came in contact with the specimens.

Result: The brass again corroded uniformly, both the copper and the zinc dissolving. There was no dezincification. The action was slower in this case than in Experiment 2. In 240 hours approximately 10 grams dissolved. The hydrochloric acid in this experiment was replaced with a fresh solution every 24 hours to prevent an accumulation of dissolved copper. Upon repetition, this experiment yielded the same results.

In Experiment 1, it was seen that if the brass were undisturbed, dezincification took place. In Experiments 2 and 3, with stirring, corrosion was complete, that is, both the copper and the zinc dissolved. If this process of dezincification were one of the selec-

tive corrosion of brass, the stirring of the solution would have no more effect than to aid the action. Why then is the dezincification stopped? It must be because the brass is first corroded as a whole and then the copper redeposited. By stirring, the copper was prevented from redepositing, by being washed away as soon as it dissolved. The action in both experiments was the same. The circulation of the solution in both cases hastened the corrosion and prevented the dissolved copper from coming in contact with the brass. It was to prevent an accumulation of the copper that the solutions were renewed daily.

The increased rate of corrosion in Experiment 2 over that in Experiment 3 is accounted for by the fact that the oxygen acts as a depolarizer, removing the hydrogen and hastening the action. Another circumstance which favors the view that the copper has been redeposited is that in Experiment 1 two distinct layers of copper were formed instead of one continuous mass. If the action had been a mere leaching out of zinc, this could not be explained. But if the action is considered as one of redeposition, it can easily be seen that the deposition of copper on both sides of the strip would leave two distinct sheets of copper when all the brass between was dissolved.

The action of dezincification can thus far be described as, first, the solution of the brass as a whole, putting the copper and zinc into solution and then the redeposition of the copper replacing the brass not the zinc alone. It is significant in this connection to note the following facts which have long been known. The potential of amalgamated zinc in acid solution is practically that of zinc. When amalgamated zinc is corroded by acids only zinc dissolves—a case of true dezincification. The potential of the alloy, amalgamated zinc, is that of the substance which goes into solution, the zinc. So, the potential of brass must be that of the substance which dissolves. The potential of brass is, however, very close to that of copper.

The point to be emphasized here, therefore, is that it is not the zinc which gives the potential to the brass, as the zinc does in the amalgam, nor is it the copper, but the substance—brass itself—acts as a separate entity with a potential of its own, capable of being replaced as a unit. Now ordinarily when copper is pre-

cipitated from solution by zinc, the action is so rapid that the deposit is the usual black spongy one. The difference in potential between the copper and the brass is so small that the action is very slow, so that the copper has the chance to deposit in the bright metallic form in which it is found.

In order to secure reasonably rapid corrosion without the use of acids, brass was used as anode with a very feeble current in different neutral solutions.

Experiment 4.

A brass strip was used as an anode in a 3 percent solution of potassium sulphate with a carbon cathode. The current density was 0.25 ampere per square foot. The time allowed was ten days.

Result: The brass strip was completely corroded. The copper was deposited at the cathode while the zinc formed a precipitate of zinc hydrate in the solution. The experiment was repeated with the same results.

Experiment 5.

A brass strip was used as an anode in a 3 percent sodium chloride solution with a carbon cathode. The current density was 0.25 ampere per square foot. The time of electrolysis was 14 days.

Result: In this case, only copper was left at the anode. Again the copper left was in the form of two thin sheets which could be pulled apart as in Experiment 1. At the cathode some copper deposited and there was a precipitate of zinc hydrate in the solution. The experiment was repeated with the same results.

Experiment 6.

Experiment 5 was repeated except that the solution was circulated by bubbling air through it.

Result: There was complete corrosion of the brass this time with no deposit of copper on the anode. The result at the cathode was the same as in Experiment 5. This experiment was repeated with the same results.

The results of these experiments are very significant. It is found in Experiment 4 that brass corrodes as a whole when used

as an anode in sulphate solution; also in Experiment 6 the brass corrodes completely in chloride solution. In Experiment 5 an apparent dezincification takes place. It must nevertheless be concluded from this that, when brass acts as a soluble anode, both the copper and zinc dissolve in their respective proportions. Experiment 5 is not, as it may seem at first glance, contrary to this hypothesis. It is noted that some copper was deposited on the cathode during the action, which means that, for some reason, the rest of it was prevented from getting away from the anode.

It is evident at least from this that there is a tendency for the brass to dissolve as a whole although some factor intervenes. The fact too, that two strips of copper, with a smooth surface between them, were found again indicated clearly that the copper remaining was redeposited (as in Experiment 1) and could not have been left behind as the result of selective electrolytic corrosion in Experiment 5. It is evident that the circulation in Experiment 6 prevents this. In other words the corrosion in Experiment 5 would have proceeded as in Experiment 6, had not something intervened to keep the copper formed directly in contact with the brass so as to cause re-deposition. Just what happened will be investigated presently. It is sufficient for the present to have shown that brass acts as a soluble anode in chloride and sulphate solutions.

Admitting then that brass is a soluble anode, if the copper which dissolves at the anode be kept in contact with or away from that anode at the will of the experimenter, it is possible to control whether or not dezincification shall take place. With this in mind Experiment 5 can be explained. A membrane of insoluble cuprous chloride which formed on the brass, kept most of the dissolved copper in contact with the brass thereby causing redeposition. In Experiment 6 when the air was blown through the solution, any cuprous chloride which tended to form would immediately be oxidized to cupric chloride and washed away. If it was an insoluble membrane of cuprous chloride which performed the function of keeping the solution of the copper salt in contact with the brass, then if an electrolyte is used in which the cuprous chloride is soluble, the formation of such a membrane should be prevented and complete corrosion should result. Two such solutions were

employed—concentrated hydrochloric acid and a saturated solution of sodium chloride.

Experiment 7.

A brass strip was used as anode in a solution of concentrated hydrochloric acid. Melted paraffin was poured on the surface of the electrolyte to prevent evaporation and water-line corrosion. The cathode was carbon. The current density was 0.25 ampere per square foot. The time of action was 10 days.

Result: The brass was completely corroded.

Experiment 8.

Experiment 7 was repeated except that a saturated solution of sodium chloride was used instead of hydrochloric acid. The time was 15 days.

Result: Again there was complete corrosion of the brass.

It is obvious from the results that the assumption made was correct. Since the vessels were sealed with paraffin, there was no chance for the air to have any effect. The result was apparently due to the fact that cuprous chloride is soluble in strong chloride solutions, so that there was no membrane present to keep the dissolved copper in contact with the brass. If the dezincification is due to the presence of a membrane, when another membrane instead of cuprous chloride is supplied, then redeposition of copper should again take place.

Experiment 9.

Brass screws were used as anode. They were screwed into white pine saturated with concentrated hydrochloric acid. The wood was used to act as a membrane; the concentrated hydrochloric acid was used as electrolyte to dissolve any cuprous chloride which may have been formed. A carbon cathode was used. The current density was 0.25 ampere per square foot. The surface exposed to air was paraffined to prevent evaporation. The time allowed was 25 days.

Results: The screws were found to be copper with a core of brass in the center, which had not yet been attacked. There was no copper at the cathode.

Experiment 10.

A brass strip was wrapped tightly with several layers of filter paper and cheese cloth and bound with string. This was done to have a membrane with which to keep the copper in contact with the brass. This strip was used as anode, and a carbon rod for cathode in a concentrated solution of sodium chloride. The current density was 0.25 ampere per square foot. The time was 21 days.

Result: When the strip was examined, the lower half was found to consist entirely of copper, while the remainder had not yet been attacked. Much of the copper from the brass was not held by the improvised membrane, but was deposited on the cathode. The copper left behind was again found in the form of two thin sheets.

These experiments substantiate the contention that, for dezincification to occur, a membrane of some sort, no matter what, is necessary to keep the copper in contact with the brass. In Experiment 4 it has already been seen that brass is completely soluble when used as an anode in potassium sulphate solution. Now if the results of Experiments 9 and 10 are true, then by merely enclosing the brass in a membrane, dezincification should occur.

Experiment 11.

A brass strip, wrapped as in Experiment 10, was used as anode in a 3 percent potassium sulphate solution as electrolyte with a carbon cathode. The surface of the solution was paraffined as usual. The current density was 0.25 ampere per square foot. The time was 16 days.

Result: The strip when removed had a brassy color on the outside, but it was found to be solid copper. This experiment was repeated twice with the same results.

Experiment 12.

An unwrapped brass strip was corroded as anode in a 5 percent zinc sulphate solution. The surface of the liquid was covered with paraffin. The current density was 0.25 ampere per square foot. The time of corrosion was 20 days.

Result: The brass corroded uniformly as a whole, with no signs of a copper deposit.

Experiment 13.

A brass strip was treated the same as in Experiment 12 except that it was bound with filter paper, cheese cloth and string to give a membrane effect.

Result: The metal remaining at the anode in this experiment was copper and some of the brass which had not been corroded.

Experiments 4 and 12 show that brass is completely corroded when used as an anode in potassium sulphate and zinc sulphate solutions. From Experiments 11 and 13, it appears that the membrane, by keeping the dissolved copper in contact with the brass caused redeposition of copper. Whether the membrane be cuprous chloride, or one artificially supplied, its function is the same, and it produces the same result—dezincification. In general, dezincification may be expected whenever the brass is so wrapped that the dissolved copper is kept in contact with it long enough to redeposit.

It is worth noting that if the only purpose of the membrane is to keep a supply of dissolved copper at the brass, then as long as there is a plentiful supply of copper in solution, no membrane should be necessary to produce redeposition. In previous experiments, electrolysis of unwrapped brass in sulphate solutions has never resulted in dezincification.

Experiment 14.

A strip of brass was used as anode in a 10 percent copper sulphate solution. A current density of 0.25 ampere per square foot was used for 14 days.

Result: Pure copper was left at the anode. This experiment was repeated twice with the same results.

Experiment 15.

Strips of brass were placed in separate solutions of cuprous and cupric chlorides for 14 days and allowed to corrode chemically.

Result: Only copper remained which again was in the form

of two sheets that could be pulled apart. The quality of the copper in this case was as tough and ductile as any copper plate obtained from an electroplating bath.

From these last two experiments, it is seen that as long as there is a plentiful supply of dissolved copper present, redeposition of the copper is obtained in spite of the fact that a sulphate solution is used. This bears out the theory that the function of the membrane is to keep the copper in contact with the brass.

SUMMARY.

The so-called dezincification can be reproduced in a few weeks in normal hydrochloric acid just as it occurs in nature in several years.

When the acid is agitated, it is seen that the brass dissolves as a whole.

The two layers of copper found in dezincified brass, can only be explained on the basis of re-deposition.

When used as anode, brass dissolves as a whole in sulphate solutions and in agitated chloride solutions.

When an insoluble membrane of cuprous chloride was allowed to form dezincification took place.

In an electrolyte in which cuprous chloride is soluble, such as concentrated hydrochloric acid or saturated sodium chloride solution, dezincification does not take place.

If another membrane is supplied in electrolytes in which cuprous chloride is soluble, then dezincification again takes place.

An artificial membrane is sufficient to cause redeposition of copper in sulphate solutions which ordinarily give complete corrosion.

Finally it was observed that when an adequate supply of dissolved copper was maintained, by using a solution of a copper salt as electrolyte, dezincification was obtained without any membrane whatever.

This investigation was undertaken at the suggestion of Dr. O. P. Watts to whom the author is indebted for many valuable suggestions in the course of these experiments.

Chemical Engineering Laboratories,
University of Wisconsin.

DISCUSSION.

F. S. WEISER[1]: The author does not mention either the composition or the physical condition of the brass used in his experiments. It is important to know its analysis, also whether it was hard or annealed, as I believe that the results may be dependent, to some extent, upon the composition and condition of the metal.

COLIN G. FINK[2]: No doubt brasses containing lead would behave differently in a sulphuric acid solution; likewise brasses containing a little tin would behave differently in nitric acid. You would get a different surface film under these conditions.

G. D. BENGOUGH and R. MAY[3] (*Communicated*): The present writers welcome heartily this paper and find themselves in agreement with most of the conclusions reached. For some years they have held the view that certain types of brass behaved as entities in initial corrosive action; i. e., that zinc-copper units took part in the action as a whole, and that copper was redeposited from solution. In the fifth report to the Corrosion Research Committee of the Institute of Metals (Journ. Inst. of Metals, 1920, **23,** No. 1) will be found some experiments carried out with cupric chloride solutions which gave results closely similar to those described by Mr. Abrams. The writers are also in agreement with the conception of the influence of membranes outlined in the paper. An interesting example of this is that a trace of arsenic in brass (say 0.04 percent) will greatly hamper so-called dezincification in sample, by forming a closely adherent layer of (probably) metallic arsenic or copper arsenide on the brass, upon which copper will not deposit; in this case the membrane hampers deposition of copper owing to its closely adherent and other characteristics, instead of encouraging it as in the case of Mr. Abrams' membranes, which were either loosely adherent or porous, and able to prevent diffusion away from the brass. In ordinary corrosion in sea water there is no doubt that the necessary conditions for deposition of copper are produced by the presence in the brass of a certain type of zinc

[1] Waterbury, Conn.
[2] Consulting Electrometallurgist, New York City.
[3] London, England.

oxy-salt, the mode of production and composition of which have recently been the subject of detailed investigation by the writers, whose results will be published shortly. They have little doubt that the main thesis of the authors, namely, that brass may behave as an entity when corroded, and that the resulting copper is redeposited, of which they have been long convinced, will, in course of time, come to be regarded as correct, in spite of almost universal rejection at the present time.

The writers do not regard the initial action of sodium chloride on brass as being the discharge of hydrogen on the brass. A report to the Corrosion Research Committee of the Institute of Metals (Sept. 20, 1922) fully discusses the initial corrosive action of sodium chloride and other solutions on brass and other metals.

O. P. WATTS[4] (*Communicated*): According to some investigators, dezincification is the result of a mere leaching out of zinc; others consider that a portion, at least, of the copper found in dezincified brass has been redeposited. Mr. Abrams has shown clearly and unmistakably the mechanism of dezincification, and has pointed out the conditions under which this dangerous form of corrosion will occur. It should now be possible, by laboratory tests such as he used, to learn whether any addition can be made to brass that will render it immune to this type of corrosion, or whether some zinc-free alloy must be employed for service where brass is now subject to destruction in this manner.

It is probably thought by most people that dezincification of brass concerns only the makers and users of condenser tubes and a few other articles with which the average man seldom or never comes in contact. The following recital of my personal experiences shows that this is not so, but that dezincification is of very common occurrence, and may not only be annoying, but even dangerous, to those who sail on salt water in small boats. My experience is with the corrosion of brass and "bronze" fittings on a small auxiliary yacht, which has contributed greatly to my joys, and occasionally to my sorrows, during the past ten years.

The first year no corrosion was apparent, but the second sum-

[4] Assoc. Prof. of Chem. Eng., Univ. of Wisconsin, Madison, Wis.

mer a friend and I had been cruising less than a week on the Maine coast when a leak developed between the head and body of a bronze pump that supplies sea water to the toilet. On attempting to tighten the brass screws which hold these parts together, the screws were twisted off. Dezincification had taken place where the screws passed through a leather valve, which was, of course, always damp.

The following year another case of dezincification was encountered. To fasten the bronze terminal of a water inlet pipe against the inside of the hull below the water line, the builder had ordered four ¼-inch bronze bolts. Observing a slight leak between this plate and the hull, I attempted to tighten the bolts; they at once twisted off because of dezincification. They were replaced by bolts turned to size from ½-inch monel rod.

The next encounter with dezincification was in the bronze lag screws which held the stuffing box on the propeller shaft against the stern post. When backing slowly from a dock the propeller struck an obstruction—not hard enough to bend the blades—yet the shock broke off both lag screws and a stream of water began to run in, so that the yacht had to be hauled alongside a wharf where she would be aground at low tide, in order to prevent her from sinking during the night. This meant a day's delay in sailing. The fractured surfaces appeared to be copper throughout. The lag screws had been in place eight years; just what fraction of this time was required to convert the half-inch bronze rod into copper, it is impossible to say from this experience.

Corrosion of brass by sea water in motion is slow; but where salt water is continually in contact with brass, and circulation is prevented by paint or some other film pervious to water, or the brass is imbedded in wood, so that the copper salts produced by the initial corrosion of the brass are held in contact with the metal, the rapid and deadly dezincification sets in.

The sheet brass used as purchased, had considerable springiness, and was evidently not in the annealed state. The screws were also tested as purchased, and probably contained the 2 to 2½ percent of lead usually added to screw-machine stock. These corroded in chloride solutions in the same manner as the sheet

brass, and I have found that machine-made brass screws suffer seriously from dezincification in sea water. It will be interesting to test Dr. Fink's prediction regarding the corrosion of lead-bearing brass in sulphate solution, and this will be done in a continuation of the study of dezincification which is now in progress.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 21, 1922, President Schlueder-berg in the Chair.

ELECTROPLATED ZINC AND THE DIFFUSION OF ELECTRO-DEPOSITS INTO ZINC.[1]

By Walter G. Traub[2]

Abstract.

Experiments were made to determine the cause of the disappearance of certain metals that had been deposited on zinc. The results indicate that copper, brass, gold and silver are diffused into zinc; whereas nickel, which does not diffuse into zinc, can be used as a preventive against diffusion of other metals deposited over it. [A. D. S.]

Several instances have been reported where thin plates of metal deposited electrolytically on zinc have disappeared after a few months. This fact seems first to have been brought to the attention of C. F. Burgess, formerly head of the chemical engineering department of the University of Wisconsin. In attempting to gold-plate some articles made of aluminum, he first deposited a coating of zinc, and then covered this with a deposit of gold. After two or three months, the party for whom he did the plating called his attention to the fact that the gold had disappeared entirely.

About a year ago, the Apollo Metal Works of La Salle, Illinois, who electroplate sheet metals on a large scale, reported trouble from the disappearance of brass and copper plate that had been deposited on zinc.

The experiments which follow were undertaken to learn whether coatings of these particular metals are diffused into zinc, or merely fall off, and in case of diffusion, what other electrodeposited metals behave similarly.

To carry out these experiments, a large number of zinc strips

[1] Manuscript received August 7, 1922.

[2] Senior in Chemical Engineering, University of Wisconsin.

TABLE I.

Electrodeposits on Zinc.

No.	Plate	Weight of Zn Strip Grams	Weight of Zn Strip + Deposit Grams	Weight of Zn Strip + Deposit After Heating Grams	Weight of Deposit Grams
1	Cu.....	21.4987	} Deposits unsatisfactory		
2	Ni.....	21.0374			
3	Cu.....	21.0982			
4	Cu.....	21.5045			
5	Ni.....	20.2197			
6	Cu.....	20.2365			
7	Brass.....	20.3709	20.4414	20.4414	0.0705
8	Brass.....	19.3744	19.4100	19.4098	0.0356
9	Brass.....	21.3318	21.3781	21.3781	0.0463
10	Brass.....	20.5427	20.5525	20.5524	0.0098
11	Cu.....	20.7171	20.7733	20.7730	0.0562
12	Cu.....	20.7626	20.9370	20.9370	0.1744
13	Ni.....	20.6561	20.7219	20.7219	0.0658
14	Cu.....	19.3450	19.4963	19.4963	0.1513
15	Cu.....	18.7269	18.8067	18.8064	0.0798
16	Ni.....	19.7058	19.9800	19.9800	0.2742
17	Ni.....	20.3665	20.6320	20.6320	0.2655
18	Cu.....	18.8304	18.9809	18.9809	0.1505
19	Cu.....	19.0864	19.0880	19.0877	0.0016
20	Cu.....	18.9690	18.9734	18.9734	0.0044
21	Cu.....	19.0140	19.0290	19.0290	0.0150
22	Cu.....	19.6371	19.6424	19.6423	0.0053
23	Cu	19.6100	19.6694	19.6694	0.0594
24	Cu	18.3009	18.3111	18.3108	0.0102
25	Brass.....	20.4950	20.5138	20.5136	0.0188
26	Brass.....	20.4380	20.4426	20.4424	0.0046
27	Brass.....	19.3645	19.3667	19.3666	0.0022
28	Brass.....	19.7490	19.7497	19.7496	0.0007
29	Brass	20.2290	20.2297	20.2297	0.0007
30	Au.....	9.8780	9.8975	9.8972	0.0195
31	Au.....	10.2237	10.2300	10.2298	0.0063
32	Au.....	10.1100	10.1132	10.1129	0.0032
33	Au.....	9.9000	9.9055	9.9055	0.0055
34	Ag.....	9.5677	} Deposits unsatisfactory		
35	Ag.....	10.5875			
36	Cu+Ag.....	10.4766	10.5500	10.5492	0.0734
37	Ag.....	11.1725	} Deposits unsatisfactory		
38	Ag.....	9.2498			
39	Ag.....	8.8972			
40	Ni+Au.....	9.5600	Good results.		
41	Ag.....	10.5600	10.5865	10.5865	0.0265
42	Ag.....	10.0919	10.1199	10.1199	0.0280
43	Ag.....	9.3700	9.4093	9.4093	0.0393

Specimens 34, 35, 37, 38, 39—very small amount of copper plus silver plate.

were cleaned in the electrolytic cleaner, dried, and weighed. These strips were then plated with different metals and alloys, such as copper, brass, nickel, gold and silver. Preliminary experiments had previously shown that these metals disappeared when plated on zinc in thin layers. The strips were then reweighed to obtain the actual amount of metal or alloy deposited. Because of limited time for observation, they were placed in an electric heater at a temperature of 60° to 80° C. for a period of two weeks.

At the end of that time, the specimens were taken out and examined. They were found to be discolored due to a thin film of oxide, which had formed on the surface. This was removed by immersion in the electrolytic cleaner. Most of the specimens then appeared like ordinary zinc strips. They were polished slightly, but the surface did not change in appearance to any appreciable extent. The deposited metals were only slightly absorbed around the edges of the strips where the deposit was thicker due to the higher current density.

The specimens were then weighed for a third time. It was found that the weight of each strip was practically the same as at the time of the second weighing just after the metal had been deposited. All specimens had been thoroughly washed and dried in all the operations to obviate any unnecessary error. Some specimens had not changed at all in weight, others had lost a few tenths of a milligram, perhaps due to the removal of the dark film spoken of above.

Specimen No. 36 was plated first with copper and then with silver. Both coatings disappeared. Specimen No. 40 was plated first with nickel and then with gold, so that a portion of the gold plate was deposited directly on the zinc. The specimen was then given the same treatment as that described above. Upon final examination it was found that the zinc had absorbed the gold in places where the gold had been deposited directly on the zinc. In places where there was a nickel layer between the gold and the zinc no change took place. Similar results were obtained with the nickel-plated zinc specimens; there was no disappearance of the deposited metal.

When plating zinc with silver, it was found necessary to use the standard silver "striking solution." This was done by first cleaning the specimen, then making it the cathode in a cell containing

the "striking solution." The anode was silver. The specimen was plunged into the electrolyte for just a brief instant. It was then washed and placed in the usual cyanide bath for silver deposition. A beautiful deposit of silver was obtained which was permanent

TABLE II.

Appearance of Specimens.

No.	Plate	Dimensions Cm.	Before Cleaning (Oxide)	After Cleaning
8	Brass...	10.3 x 4	dark gray	gray
10	Brass...	10.9 x 4	dark gray	gray
11	Cu.....	11.1 x 4	grayish brown, edges brown	grayish brown mottled
12	Cu.....	10.3 x 4	same as No. 11	gray, brown edges
13	Ni.....	9.7 x 4	not affected	not affected
14	Cu.....	9.9 x 4	gray, reddish brown edges	gray and brown, mottled
15	Cu.....	10.1 x 4	same as No. 14	same as No. 14
16	Ni.....	9.8 x 4	not affected	not affected
17	Ni.....	9.7 x 4	not affected	not affected
18	Cu.....	10.4 x 4	brownish	gray and brown
19	Cu.....	10.3 x 4	gray, brown edges	gray
20	Cu.....	10.3 x 4	same as No. 19	gray
21	Cu.....	10.3 x 4	gray, purple edges	gray
22	Cu.....	10.2 x 4	same as No. 21	gray
23	Cu.....	10.5 x 4	brown and purple	gray, brown edges
24	Cu.....	10.4 x 4	gray, purple edges	same as No. 23
25	Brass...	11.9 x 4	brown, reddish	gray
26	Brass...	11.6 x 4	same as No. 25	gray
27	Brass...	11.7 x 4	gray, brown edges	gray
28	Brass...	11.6 x 4	yellowish gray	gray
29	Brass...	11.8 x 4	yellowish gray	gray
30	Au.....	11.5 x 4	gray	gray
31	Au.....	5.2 x 2	very dark gray	gray, silvery
32	Au.....	5.9 x 2	grayish black	gray
33	Au.....	5.9 x 2	grayish black	gray
36	Cu+Ag.	11.6 x 2	gray	gray
41	Ag.....	11.3 x 2	gray	gray
42	Ag.....	12.0 x 2	gray	gray
43	Ag.....	10.8 x 2	gray	gray
40	Ni+Au.	.....	.....	gray where Au directly on Zn; with layer of Ni between, no change

and did not come off by rubbing or by wear, but was absorbed on heating.

The nickel plates were deposited from a solution designed especially for the direct nickeling of zinc. The solution contained

sodium citrate. The gold, silver, brass, and copper were, of course, deposited from cyanide solutions.

These experiments show conclusively that thin plates of copper, brass, gold, and silver are diffused into zinc. Nickel is not diffused into zinc, and it can act as a preventive against diffusion of other metals deposited over it.

Chemical Engineering Laboratories,
University of Wisconsin.

DISCUSSION.

H. M. WILLIAMS[1]: I noticed this same phenomenon about two years ago. There was a name plate manufacturer who had substituted zinc sheet for brass on account of the difference in price. The zinc was plated with brass and copper for the various color effects. The plated sheets were placed in storage and in less than six months the plate had entirely disappeared. It would have been well if this investigation had been followed up with some micrographs. Probably that would have proven the theory advanced in the paper.

WM. BLUM[2]: Two or three years ago we had an inquiry from a manufacturer who had used brass plated zinc for electric light fixtures. With the unfavorable conditions caused by the elevated temperature on certain parts of the fixtures, absorption of the brass took place in a very short time.

The question is often asked, "Is the adhesion of an electrodeposit to the base metal due to alloying?" It seems at least possible that if this alloying does take place slowly between certain metals, there may be incipient alloying as soon as the one metal is deposited on the other.

R. J. MCKAY[3]: I believe you will find that this difference is a difference in rate, rather than an absolute difference, in the case of nickel, in view of a similar occurrence in the metallurgy of

[1] Research Engineer, General Motors Res. Corp., Dayton, Ohio.
[2] Chemist, Bureau of Standards, Washington, D. C.
[3] International Nickel Co., New York City.

nickel. In electrodeposition, if the current is shut off, the cathodes will take on a rosy color, due to the cementation of a slight amount of copper out of the solution. If these cathodes are then raised out of the solution and stored for a few months, the rosy color has entirely disappeared, probably due to the diffusion of the copper into the nickel; but this rate is very slow, and if the deposit is thick the color remains.

A deposit of copper on nickel will diffuse very rapidly at temperatures of cherry red and low red heat.

A. G. REEVE[4]: It might be interesting to say in this connection that we noticed quite a number of years ago in the case of certain ornamental objects stamped out of pure block tin plated with gold, upon these objects subsequently lying around, the plating was not worn off, but in the course of a year or two it completely disappeared. We assumed that the gold was absorbed in some way.

MEMBER: Regarding the junction of the tin and iron, if the tin is put on by the standard hot process there is considerable alloying. In our tinning work, we find that when the tin left in the iron amounts to about 0.3 percent, so-called "flowers" appear; that is, the tin that is left on is alloyed with the iron and forms figures in the form of flowers.

We have carried out some experiments in putting tin on iron electrolytically, and upon taking the tin off, the flowers do not appear. Of course the electrolytic deposit is put on only a short time before being removed, so that in time there may be an alloying feature. In that case, however, the tin apparently does not alloy appreciably with the iron electrolytically, while it does when deposited hot.

W. H. FINKELDEY[5] (*Communicated*): Mr. Traub's interesting paper recalls several similar experiments which were made in our laboratory a few years ago. We became interested in the absorption of zinc base electrodeposited metallic coatings during the course of an investigation to determine the reasons for the disappearance of plated coatings on spun and drawn zinc articles. Our experiments were confined entirely to electrodeposits of copper, inas-

[4] Research Dept., Oneida Community Ltd., Kenwood, N. Y.
[5] Research Division, New Jersey Zinc Co., Palmerton, Pa.

much as it is a rather general practice in the plating industry to coat or flash zinc articles with copper previous to plating with other metals. We were interested in determining whether there was an absorption of the copper plate and, if it did take place, its approximate rate. There was considerable doubt in the minds of several manufacturers who were plating zinc articles, whether the possible absorption of the copper flashing might not materially influence the adhesion of subsequent electrodeposited coatings. In some cases they considered it to be the cause of serious peeling and blistering.

Briefly, our experiments consisted of electroplating specimens of strip zinc with three thicknesses of copper plating, exposing the same to temperatures ranging from 60° to 400° C. and noting the time required to produce total absorption of the copper plating. The thickness of the copper plate coatings are given in Table I.

TABLE I

Specimen No.	Weight of Copper g./sq. cm.	Thickness of Copper Plate in cm.
1	0.00026	0.000029
2	0.00030	0.000034
3	0.0037	0.0038

The results of our experiments are given in Table II.

TABLE II

Specimen No.	Thickness of Copper Plate in Cm.	Length of time after which absorption was complete at									
		400°C Min.	350°C Min.	300°C Min.	250°C Min.	200°C Min.	150°C Min.	125°C Min.	100°C Hr.	75°C Days	60°C
1	0.000029	1	1	2	2	5	15	40	4	2	(*b*)
2	0.000034	1	1	2	3	7½	25	90	5	2	. . .
3	0.0038	3	5	15	25	140	7 Ds.	. .	(*a*)	. . .	. . .

(*a*) Not after one month. (*b*) Not after one week.

Our experiments with copper plating confirm those of Mr. Traub, and we agree with the conclusions which he has drawn. However, there is one point which we wish to bring out. In the case of a copper plate, the rate of absorption is dependent to no

little extent upon the thickness of the copper plate, since the diffusion rate will be materially lowered as the surface of the zinc metal under the coating becomes richer in the constituent which is being absorbed. Thus we noted from our experiments that our heaviest plated coatings were not absorbed after heating at 100° C. for over one month. As would be expected, the rate of absorption is greatly influenced by the temperature. At a higher temperature, absorption of the thinner coatings was completed in some instances within a few minutes.

From our examinations of actual plated articles which had previously been flashed with a coating of copper, we could find no indication that peeling was due to any absorption of the underlying copper plate. In many instances, where the plated coating could be peeled off, the underlying copper flashing was found to have peeled from the zinc base and to be tightly adherent to the outer coating.

It is apparent, also, that trouble resulting from diffusion of plated coatings can be overcome to a considerable extent by increasing the thickness of the copper flashing which is usually deposited preparatory to the finished plating.

The writer has recently examined microscopically a number of nickel plated zinc sheets of German origin, which were several years old, in which the "flash" coat of copper is still clearly visible. This material carried a copper coating of 0.024 g./sq. dm. over which had been deposited a nickel coating of 0.204 g./sq. dm.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 21, 1922, President Schlueder-berg in the Chair.

THE EFFECT OF SINGLE IMPURITIES ON THE ELECTRODEPOSITION OF ZINC FROM SULPHATE SOLUTIONS.[1]

By John T. Ellsworth[2]

Abstract.

This research sets forth the limiting value of each ordinary impurity which may be present in a zinc sulphate solution without seriously affecting the cell efficiency. The presence of impurities as Cu, Mn, Cd, Fe, Sb, Co, and CaO were investigated singly, under conditions as nearly commercial practice as possible. Conditions other than those pertaining to the direct effect of each impurity and affording opportunity for further experimentation, were eliminated in these tests. [A. D. S.]

It has been recognized ever since commercial electrolytic zinc plants have been in operation, that zinc can be deposited economically from sulphate solutions only when these solutions consist as nearly as possible of pure zinc sulphate. In the electrolyte made from complex western ores there are usually several other soluble metals in varying quantities, and while occasionally one particular impurity will predominate and its effect on the cell action appears to be clearly marked, there has always been the possibility that this effect might be due to a particular combination of reactions of more than one element.

The purpose of the experiments which are described by this article was to get a definite idea of the effect of each one of the ordinary impurities, taken singly. In preparation for this a series of runs were made on a practically pure zinc sulphate solution, in order to establish a basis of comparison with the impurity tests under the conditions of solution strength, current density, tempera-

[1] Manuscript received August 19, 1922.

[2] Park City, Utah.

ture, time of deposition, and general cell conditions which it was thought best to use; as variations in all these conditions have their effect on the zinc deposit.

An absolutely pure zinc sulphate solution is, of course, practically impossible to obtain without a great deal of arduous preparation, which was not considered necessary for this particular series of tests, as they were to be made more for their commercial application than for the purely scientific data which might be obtained. The solution was therefore prepared by dissolving Judge electrolytic zinc (99.95 percent Zn) in pure sulphuric acid. In order to hasten solution, the zinc pieces were connected by copper wires to carbon sticks, also placed in the acid. This had the desired effect, but resulted in a small amount of copper, formed as sulphate from the fumes, dropping into the solution, as the wire had not been covered carefully enough. A part of the zinc was reduced to borings and oxidized in an assay muffle. A little iron was picked up from this operation. The solution was treated once with very fine zinc dust and filtered, and while not absolutely pure, all the impurities present were considerably below the amounts where their presence could cause cell trouble. The analyses of the following three carboys are representative of the entire solution used. The amounts are given in grams per liter.

Carboy	Zn	H_2SO_4	Mn	Cd	Cu	Fe	Co	SiO_2	Sb	CaO	MgO
1	98.8	0.00	0	0.0006	0.0018	0.001	0	0	0	0	0
2	102.6	0.41	tr.	tr.	0.0011	0.0006	0	0	0	0	0
3	105.3	0	0	tr.	0.0019	tr.	0	0	0	0	0

PURE SOLUTION TESTS.

As a basis for comparison of the effects of the different impurities it was necessary to determine a definite set of conditions to be held throughout the series. Electrolysis was carried on in rectangular lead cells, which contained approximately 11.5 liters of electrolyte. Electrode spacing was 2 inches (5.1 cm.) between centers and the general arrangement the same as in the usual commercial plant. Cathodes were of ⅛-inch (0.32 cm.) aluminum and anodes of 3/16-inch (0.48 cm.) chemical lead, and contacts between plates and electrode bars were tinned to prevent partial

insulation; bus bar contacts were loose, that is, merely held by the weight of the electrodes. There were two 6 by 10-inch cathodes (15.2 x 25.4 cm.) and three 5½ by 9½- inch (14 x 24 cm.) anodes in each cell, these dimensions being the portion of the plates actually in the solution. Temperature of electrolyte varied between 19° C. and 26° C. for nearly all runs except in cases of severe re-solution or of high current density. While this is a lower temperature than in the usual commercial plant cells, its use obviated the necessity of externally applied heat, thus tending to reduce variable conditions as much as possible. Increased temperature in the zinc cell lowers its resistance and thus increases the power efficiency, but when impurities are present it also accelerates their harmful reactions in a much greater proportion than its action is beneficial on the zinc alone.

A solution strength of about 100 grams per liter was used because, although this is higher than in most commercial plants, it is about the proper strength to use with normal temperatures, provided that sulphate losses in filtering residues can be avoided. At around 125 g./L. zinc sulphate begins to crystallize out and would give trouble in filter cloths and pipe lines. It is best to use as high a zinc content as possible in order to carry the minimum amount of solution in the cycle.

Current densities of 5, 15, 20, 25 and 50 amperes per square foot (45, 135, 180, 225 and 450 amp. per sq. dm.) were tried. The usual commercial low density work is somewhere around 20-25 amp. sq. ft. (180-225 amp./sq. dm.). By holding an even current on these cells, the density could be increased from 25 to 50 by merely taking out one of the two cathodes. This gave a definite idea of the relative effect of these densities with as little chance of altering other conditions as was possible.

The usual time of deposit in commercial work is 48 hours. This could not be held through this test work on account of limited apparatus, time consumed for individual tests, difficulty in preparing the pure solution, etc. It was therefore necessary to divide the runs into 8-hour periods. On account of the effect of cell gases on the deposit, as hereafter explained, it was not always advisable to remove the cathodes or cut off the current at all of such periods. However, this was done often enough to approximate the relative efficiency of the different periods.

The results of these preliminary runs were as follows:

(a) A test was first made to check zinc analyses with specific gravity measurements and on the minimum zinc depletion allowable for good cell efficiency. Densities of 15 and 25 amp. per sq. ft. (135 and 225 amp./sq. dm.) were used. It was found that the usual zinc determination with ferrocyanide on solutions of this strength were not accurate within about 2 percent. When the zinc in the electrolyte is reduced to about 20 grams per liter, corresponding to a specific gravity of 1.08, the amount of gas increases greatly and the current efficiency is lowered considerably. This is probably due to lack of the proper proportion of zinc ions for the current strength. An attempt was made to check roughly the relative ionization by freezing point tests, but these were not very satisfactory. While in general the freezing point was lowered with increased acid, the difference did not seem to be altogether proportional to either acid increase or zinc depletion.

TABLE I.

Solution During Electrolysis.

Volts	H_2SO_4 g./L.	Sp. gr.	Freezing Point °C.
5.00	22	1.240	— 5.5
3.75	72	1.194	—11.5
3.65	78	1.196	— 7.2
3.50	92	1.192	— 8.0
4.50	19	1.223	— 4.0
3.45	84	1.160	—11.5
3.30	105	1.139	— 8.0
3.35	127	1.119	— 8.3
4.00	20	1.241	— 5.0
3.75	35	1.230	— 5.4
3.50	56	1.202	— 6.5
3.35	74	1.201	— 7.3
3.30	84	1.200	— 7.5
3.25	91	1.196	— 9.0
3.25	105	1.192	— 8.5

During these tests the acid strength was varied from zero to about 125 grams per liter, and voltages varied in proportion to acid strength from 5.0 to 3.2. Current efficiency would hold at about 100 percent with low acid for 20 to 24 hours, and averaged,

except in case of very low zinc content, well above 85 percent for periods of from 40 to 48 hours.

(b) The effect of very low current density was shown by three cells connected in series, the first of which was a compartment cell with pure asbestos diaphragms filled with neutral solution, and the other two were undivided cells with fairly high acid electrolyte from the previous tests. Solution was fed to the cathode compartment of the divided cell and the overflow of each was discarded. Each cell was supplied with enough fresh solution to satisfy current requirements at 100 percent efficiency. A current density of 5 amp./sq. ft. was held for 24 hours.

TABLE II.

Effect of Low Current Density.

	Acid (start)	Sp. gr. start	Acid end	Sp. gr end	Volts av.	Current Efficiency Percent	Temp. av. °C.
Anode comp. No. 1..	0	1.258	20	1.250	3.40	..	12-15
Anode comp. No. 2..	0	1.258	20	1.249	3.40	..	12-15
Cathode comp.....	0	1.258	11	1.224	3.40	100	12-15
Cell No. 2.....	118	1.141	109	1.153	2.90	3	12-15
Cell No. 3.....	117	1.148	109	1.160	2.90	7	12-15

The results as shown by Table II are almost self-explanatory. The voltage was reduced on the acid cells to a point where the local effect of the Zn-Pb E. M. F. would dissolve off the zinc almost as fast as it was deposited.

(c) A test was made with density of 25 amp./sq. ft. (225 amp. /sq. dm.) as in the previous test, starting the electrolysis with neutral solution and allowing it to proceed until distinct re-solution appeared.

TABLE III.

	Acid Start	Sp. gr. Start	Acid end	Sp. gr. End	Time Hours	Current Efficiency Percent	Temp. °C.
Anode No. 1..	0	1.24	79	1.217	35	....	22
Anode No. 2..	0	1.24	89	1.191	35	....	22
Cathode	0	1.24	73	1.116	35	86.3	22
Cell No. 2.....	0	1.24	129	1.110	39.7	79.0	22
Cell No. 3.....	0	1.24	138	1.110	39.7	97.3	22

The comparatively low efficiency in No. 2 cell was due to a poor bus-bar contact on one plate. The shorter time of deposit in No. 1 cell was due to the smaller number of zinc ions available to the cathode, the diaphragms allowing comparatively easy passage of hydrogen ions but less easily of the zinc ions.

(d) A test was then made to show the effect of high acid without undue depletion of zinc.

TABLE IV.

	Density amp./sq. ft.	Acid av.	Volts av.	Current Efficiency Percent
Cell No. 2.....	30	175	3.15	82.1
Cell No. 3.....	15	250	3.05	85.0

In this run the effect of local resistance difference between plates was shown. In cell No. 3 56.5 percent of the zinc was on one cathode, although the other plate showed no sign of re-solution and the average cell efficiency was good.

(e) The effect of higher temperatures and densities was also tested. The former lowered the resistance of the electrolyte, and therefore increased power efficiency on temperatures around 50° C. by 5 or 10 percent, although there was very little difference in ampere efficiency. Higher density in general slightly improved ampere efficiency, although, in order to keep the voltage down, this must be accompanied by higher temperatures or acid strength, or both. The effect of the increased density seems to be on the action of the gas bubbles. These vary considerably under different conditions. In case of very low acid they are usually finely divided, and free themselves immediately from the cathode surface; with medium strength acid and low density they are larger and hang longer to the plate; and with high acid and high density they are formed rapidly and are freed easily.

There are probably certain proportions between number of zinc ions, acid ions, and amperes used, which govern the physical characteristics of these bubbles, but this would be difficult of demonstration. The fine, rapidly moving bubbles leave the smoothest zinc deposits and in such cases the highest current efficiency is obtained.

It is probably the action of these bubbles carrying off minute particles of zinc before they are firmly included in the deposit, together with the occasional dissolving of zinc by local opposite E. M. F., and the use of current to produce hydrogen in excess of that required by the acid, which accounts for the difference between the efficiencies obtained and 100 percent.

A careful study of these conditions would probably result in improved cell practice, as the fact that practically 100 percent efficiencies were obtained in several instances during the pure solution tests indicates that such good results could be approximated commercially, once the reactions were thoroughly understood.

The net result of these pure solution tests was to show that with sufficient zinc ions present, fairly high acid strength, not too low current density, and with reasonable attention to contacts, etc., an efficiency of between 90 and 100 percent could be expected for deposits of less than 24 hours and of between 80 and 90 percent for deposits of between 24 and 48 hours. The tests also indicate that the so called overvoltage of hydrogen on zinc is a variable quantity with the different conditions as outlined. The effect of opposite E. M. F., as mentioned, may be partially or entirely due to this overvoltage, but, if so, it is a very variable quantity indeed and, if a constant for sulphate solutions of this strength its effect is negligible or no 100 percent efficiency could be obtained.

IMPURITY TESTS.

With the preliminary runs completed to show the effect of general conditions, some of the ordinary impurities were added separately to pure solution; the chief object being to find the amounts of such impurities which would be allowable without serious effect on cell efficiency.

Copper. Amounts of copper in solution up to around 0.020 gram per liter do not have a serious effect on 24-hour metal, and the maximum for 48-hour metal is between 0.010 and 0.015 gram per liter.

The first effect as the copper increases is to form needlelike sprouts before the dark color of the copper appears. As the amount of copper is still further increased, the deposit becomes

black and spongy, and current efficiency decreases rapidly. If a large enough amount of copper is present, it alone will deposit and practically no zinc will appear on the cathode.

Current density of 50 amp. per sq. ft. (450 amp. per sq. dm.) raises the efficiency about 5 percent over that of 25 amp. per sq. ft. (225 amp. per sq. dm.) on the smaller amounts of this

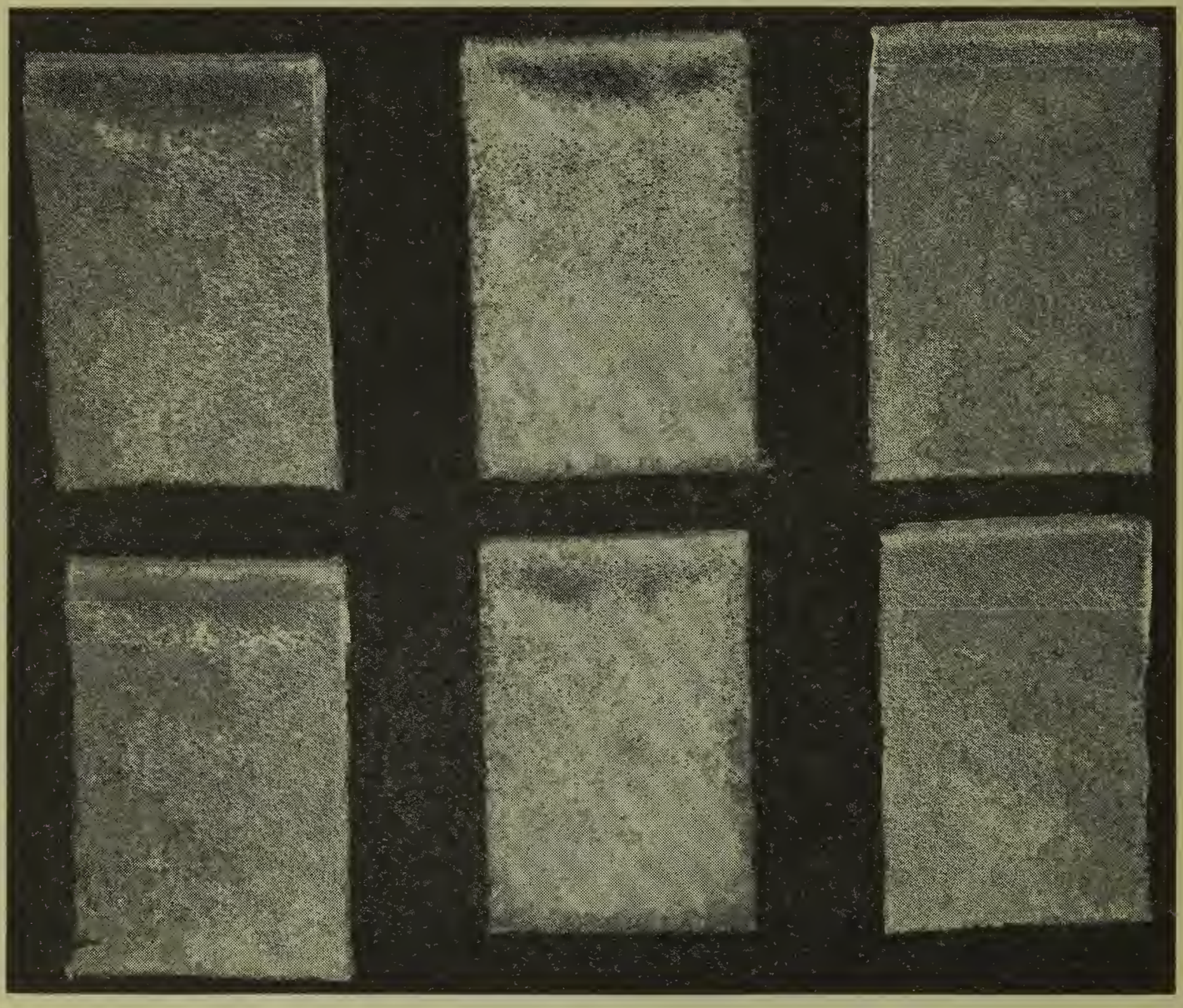


Plate "B"

impurity. General appearance of cathodes are shown by plate "B".

Manganese. Manganese has no serious effect on the zinc deposit up to amounts of approximately 1.0 gram per liter. When present in this or higher amounts, small particles of manganese dioxide remain suspended in the electrolyte, and a part of these

become imbedded in the zinc deposit. As these are saturated with electrolyte, as soon as they are covered with zinc an individual cell is formed; the zinc which has formed over the particle of manganese dioxide becoming a soluble anode. The general effect of this action is to produce holes in the zinc which enlarge with age of the deposit, as per plate "C".

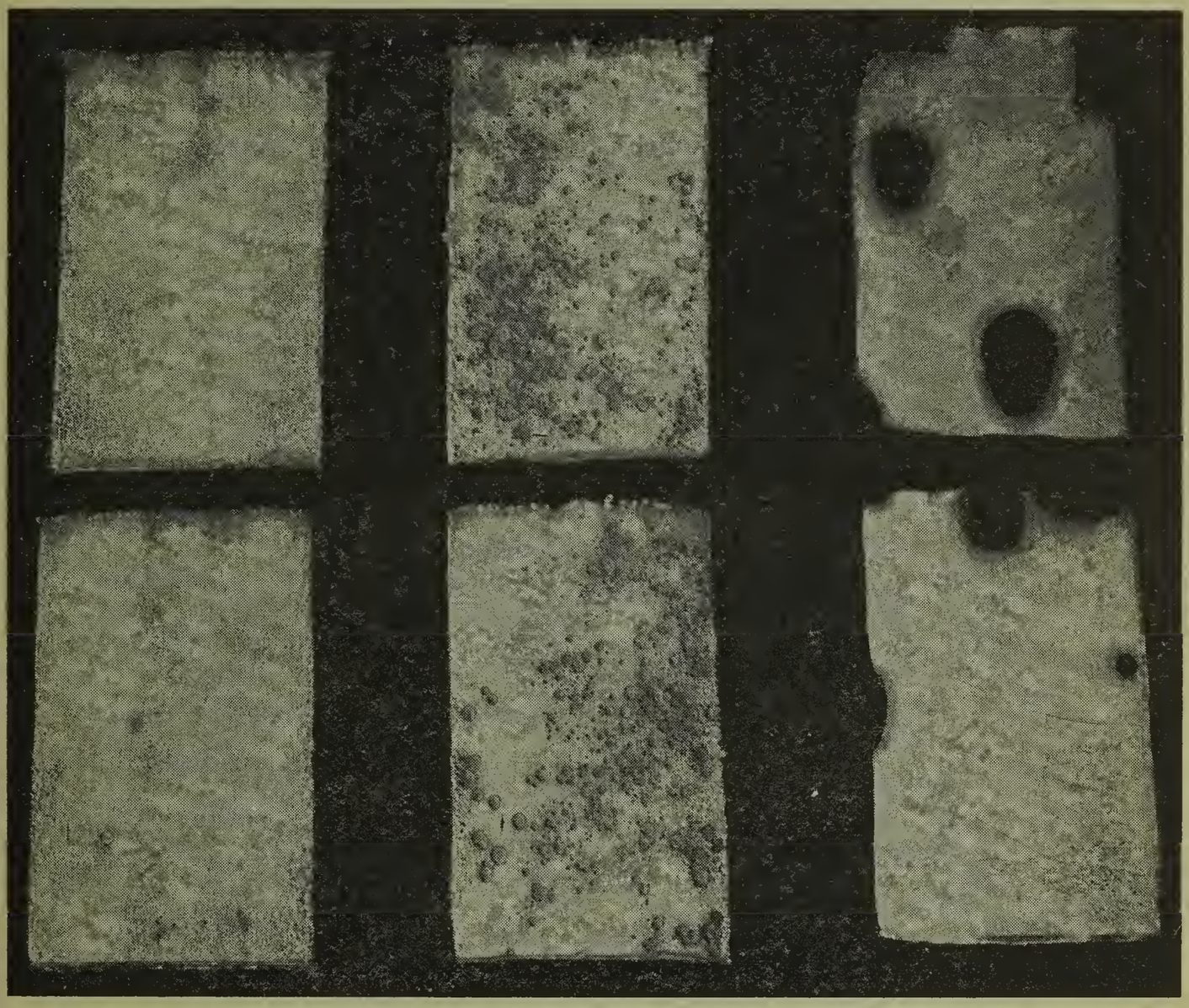


Plate "C"

With the amount of manganese raised to 12 or 14 grams per liter no zinc at all was deposited.

Cadmium. This impurity, up to certain limits, is a distinct help to the deposition of zinc. One deposit of 56 hours with the amount of cadmium in the solution gradually increasing to 0.09 gram per liter showed a current efficiency of 95 percent. Most of the cad-

mium deposited with the zinc. A 24-hour deposit from solution containing approximately 0.50 gram per liter gave a current efficiency of 90 percent.

This amount of 0.50 gram per liter is about the maximum allowable for fair efficiencies on 48-hour metal. When this amount is exceeded the deposit becomes rough and black. The general appearance of the cathodes is shown by plate "D".

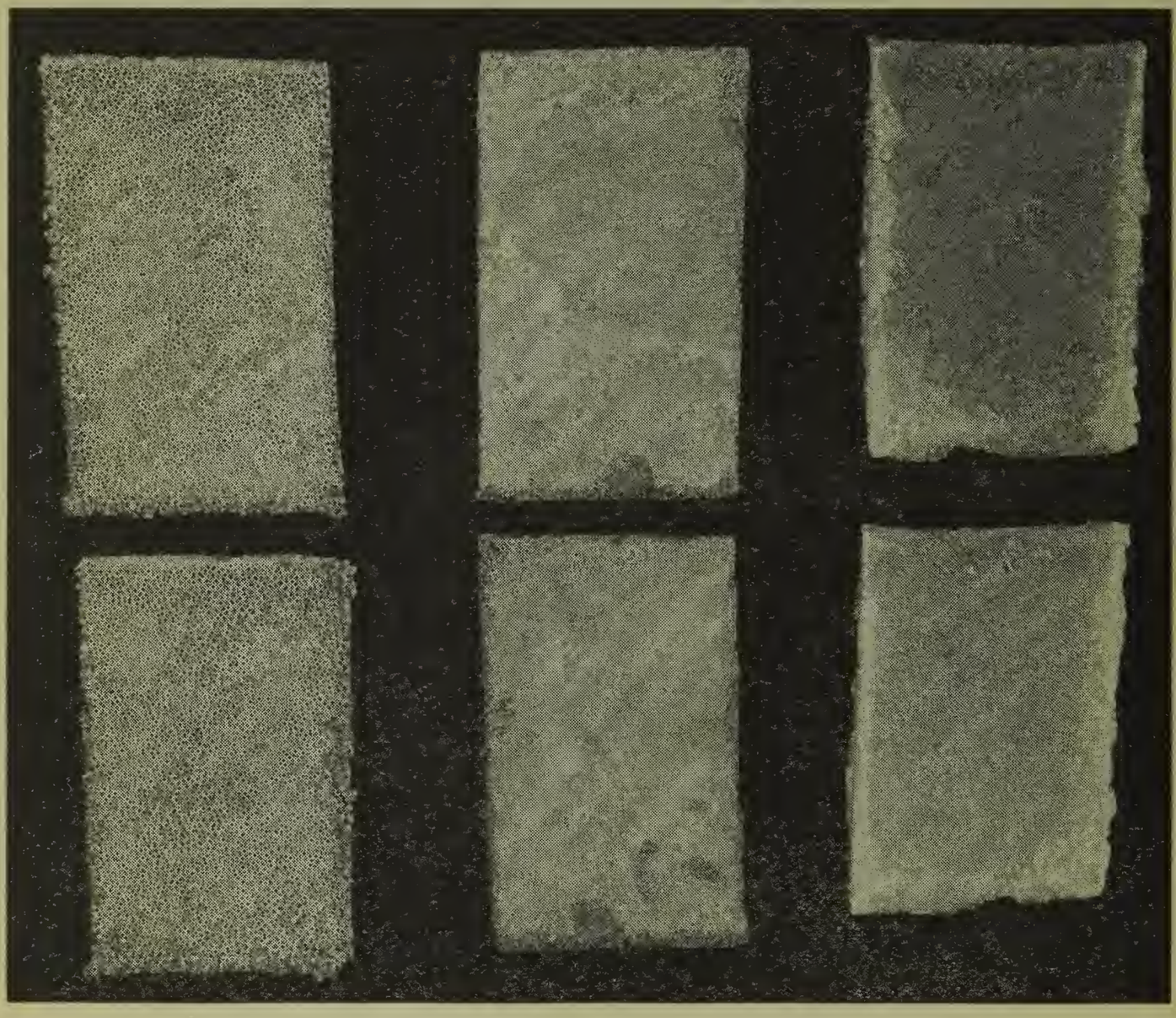


Plate "D"

Iron. This impurity does not deposit, but uses up current in being alternately oxidized and reduced. About 0.05 gram per liter is the maximum amount allowable before much effect is shown on current efficiency. The zinc deposit is particularly smooth and bright with amounts of iron below this maximum.

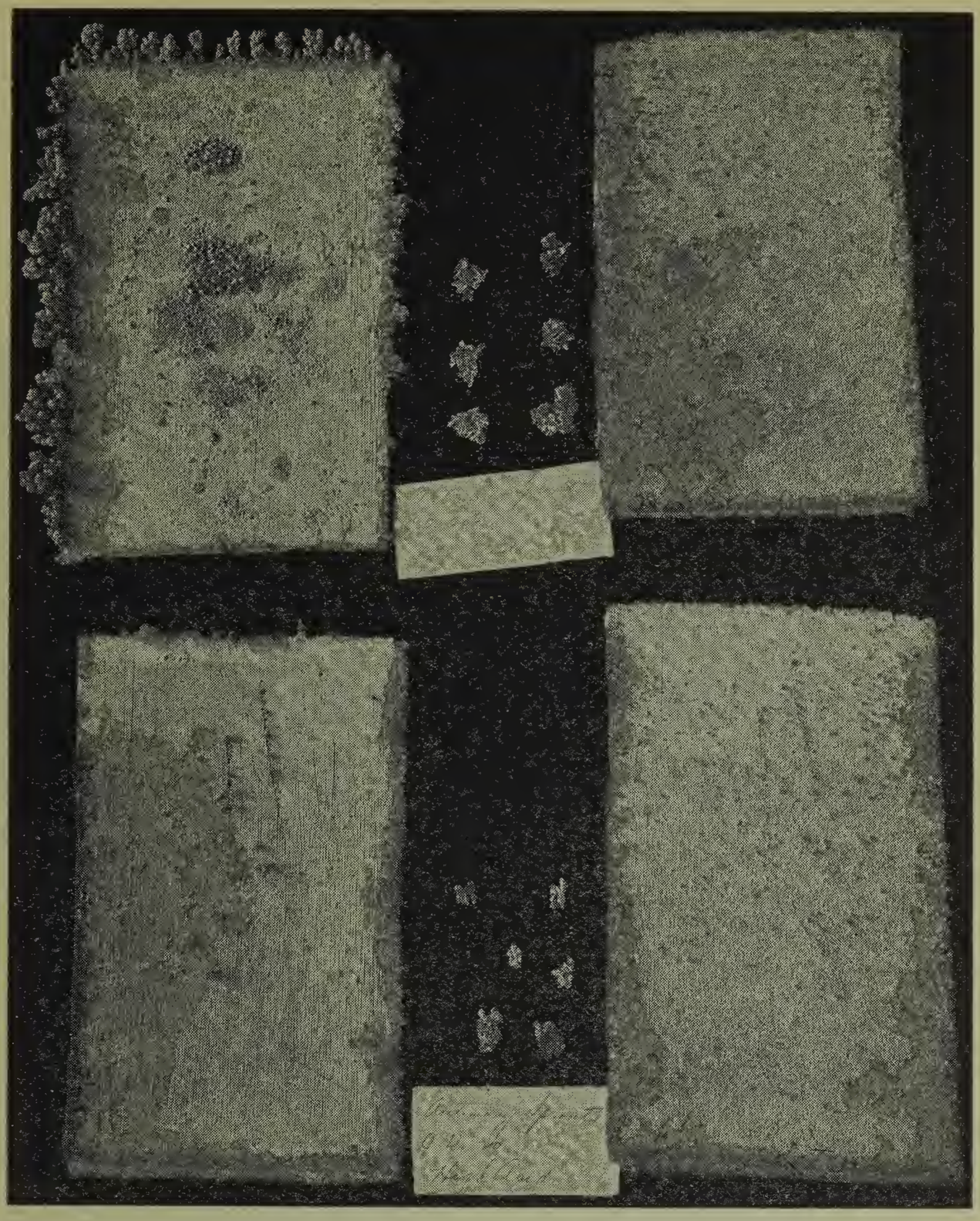


Plate "E"

Antimony. The effect of antimony is the most serious of any which were tried. One milligram per liter, or a little less, is the maximum allowable amount for 48-hour deposits. In amounts of 2 milligrams per liter, or more, it forms very distinctive, tree-like sprouts, and the zinc deposit, in addition to giving a poor effi-

ciency, is soft and spongy and hence hard to melt. In amounts below 2 mg./L. the sprouts are not as distinctive but efficiencies are poor until the maximum of 1 mg./L. is reached. The general appearance of deposit is shown by plate "E".

With manganese also present in the electrolyte the harmful effect seems to be increased, so that in the ordinary plant cell solution the maximum allowable amount of antimony is about 0.7 mg./L., or 7 parts per 10 million.

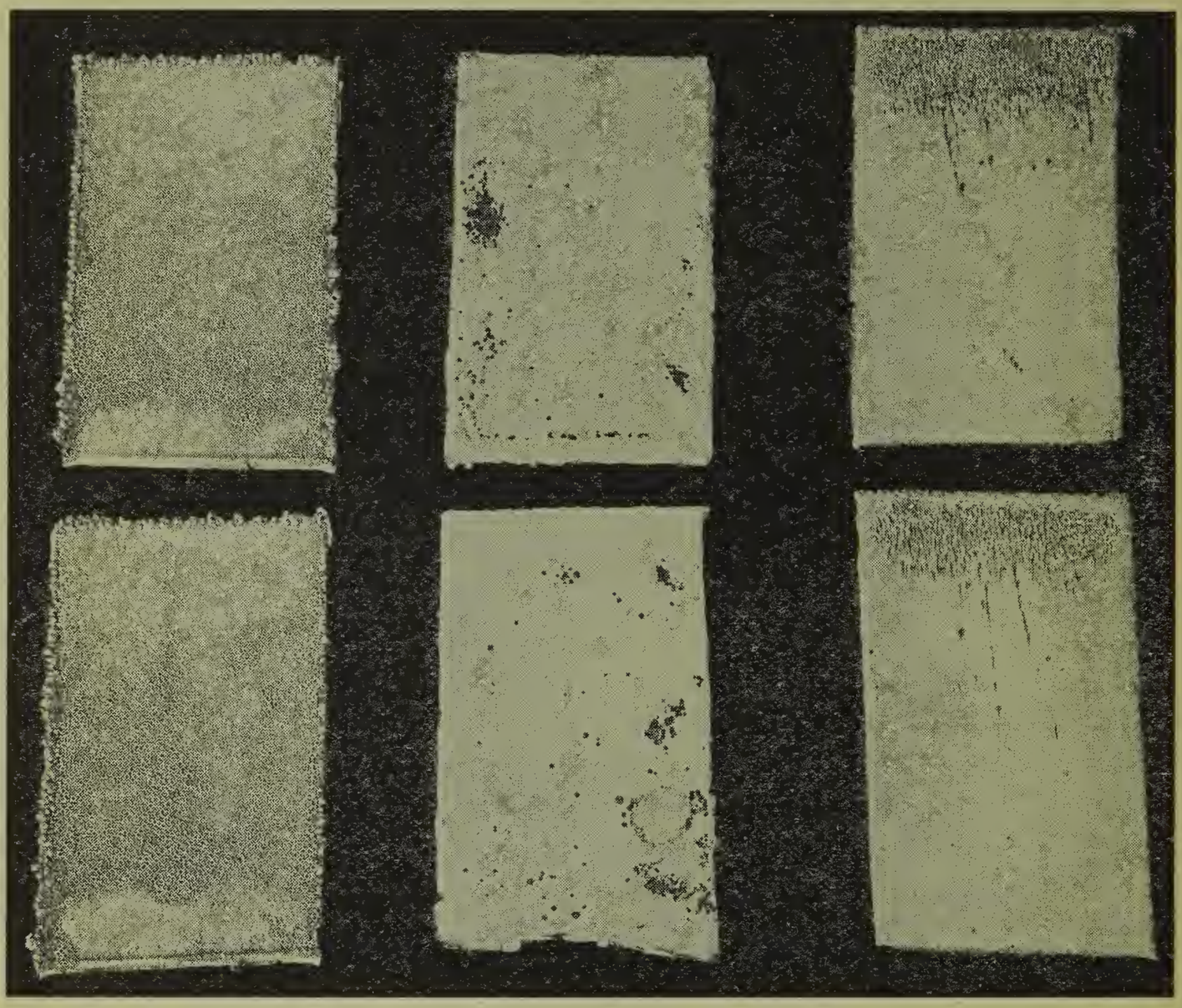


Plate "F"

Cobalt. The limiting amount of this impurity allowable for good efficiency is about twelve milligrams per liter (0.012 gr./L.). The effect seems to be something like both the high manganese and iron. This deposit also has a distinctive appearance, and is shown by plate "F."

Lime. The effect of certain quantities of lime appears to be purely physical, and is one which has generally been confused with some of the more metallic impurities. The saturation point of CaO in these zinc sulphate solutions apparently varies between 0.70 and 1.0 gram per liter. As the cell increases in acid a solution, which may be slightly super-saturated with calcium sulphate at the beginning, will become entirely clear, but when the usual cascade of five or more cells is used the evaporation of electrolyte may overcome this effect, and the solution become super-saturated again at the lower end of the cascade in spite of the high acid content.

A part of this sulphate of lime will deposit on the sides of the cell, but, as the direction of circulation is chiefly toward the cathode, a considerable amount will deposit there. Whenever it does so, the zinc becomes soft and spongy, particles of zinc fail to adhere to the plate, and current efficiency is seriously impaired.

SUMMARY.

A higher current density than 50 amp. per sq. ft. was not used because the beneficial effect of raising the density from 25 to 50 amp./sq. ft. (225-450 amp./sq. dm.) was so slight that it did not seem that further increase would be of enough benefit, as far as commercial operation is concerned, to overcome the disadvantages of the use of very high acid, the more rapid deterioration of electrodes, etc. It is necessary that density be high enough to overcome differences in conductivity at the cathode surface, insuring deposition over the entire plate. It is evident that the higher the acid content of the electrolyte, the higher this density must be; but as good power efficiencies can be obtained with densities of around 25 amp./sq. ft. as with 100, provided the proper electrolyte is used.

Aside from the variations in current efficiency shown in the pure solution runs, the most interesting point developed was the characteristic type of deposit given by each impurity taken singly. So far as possible, the effect of rapid re-solution after the critical percentage of impurity was reached was avoided, as this gives blackened, spongy metal, which has much the same appearance irrespective of which impurity or impurities was the original cause of the trouble. Thus a 24-hour deposit from solution containing about 1.1 grams per liter CaO showed a spongy, lacy deposit,

which looked about the same as one of the same length of time containing 1.5 milligrams per liter of Sb. The difference was that the antimony deposit, during the first 8 or 10 hours, was quite firm and smooth, while that obtained from the solution containing CaO was soft and the efficiency low from the start. Aside from the knobs and warts produced by the hydrogen bubbles, only two definite growths were shown. These were by the antimony which was a tree formation with a pin-point base, and the copper, which were very fine, sharp-pointed projections, not easily distinguished by the naked eye. The holes produced by the manganese as a single impurity are quite typical of plates observed in commercial cells.

No serious attempt is made to explain thoroughly the action which produces each of these various types of deposit, or the variation in efficiency obtained from the pure solution runs. To do so would require many additional experiments, which might or might not be of practical value. However, the results obtained suggest certain conclusions which may be amplified or partially contradicted by more detailed work.

1. The overvoltage of hydrogen on zinc does not have a serious effect on current efficiency in such solutions, except in that the adherence of the bubbles to the cathode alter the surface of the deposit. As this becomes older the roughness increases, the current is less evenly distributed, and efficiency decreases. However, the amount of power consumed by the formation of hydrogen alone is a negligible quantity.

2. The general statement that the harmful effect of impurities is due to the difference between their respective over-voltages of hydrogen and that of zinc seems questionable. While, at first, this seems a reasonable explanation, it must be remembered that re-solution of zinc from any cause always results in excessive generation of hydrogen. It may be true that in some cases falling off of efficiency is preceded by excessive production of hydrogen, but in a good many cases it is not true. For instance, in the case of iron present around the critical amount of 0.05 gram per liter, no more hydrogen was observed escaping from the cell than with pure solution. The deposit was exceptionally smooth and bright, and the current efficiency was materially decreased.

Even in the case of metals which actually deposit, such as copper, it does not seem that the small amount of such deposit could divert enough current for this action alone to be responsible for the large amount of damage which a very small amount of impurity can cause. It is not intended by this statement to belittle any of the great amount of work which has been done to obtain data on various phases of "overvoltage", but only to suggest that, in some instances, it may be possible to give a clearer explanation of certain cell reactions than by the use of such a general term.

3. It would seem more advisable to ascribe the cause of the ordinary harmful effects observed in commercial practice either to mechanical effects, such as undue roughening of the zinc deposit by irregular patches of metals which deposit on or by substances like manganese dioxide which are included in the zinc, or to alternate oxidation and reduction effects, which in case of the metals arsenic and antimony may easily form a cycle of reactions which will proceed rapidly enough to consume considerable current or to start re-solution of the zinc deposit.

More than the limiting amount of antimony may sometimes be fed to a cell which is working well, and the antimony content of the electrolyte brought up over the danger point for several hours before the harmful effect is observed. In this case a considerable amount of the antimony is found in the cell residue (manganese dioxide). It would be impossible to start a cell with an equal amount of this impurity and hold an equally good current efficiency.

In cases of continued zinc re-solution the lead anodes become coated with a white film, which would indicate reduction of the usual peroxide to oxide of lead.

In the case of manganese it is not likely that the metal is deposited at all, but several compounds are formed from the sulphate of manganese which enters the cell. Of course, the limiting amount of this impurity is quite high, but in the proportion of 1 Mn : 7 Zn no deposit at all was formed on the cathode.

4. As no colloid additions were made in any of these tests, it might give a better idea of the actual reactions of the impurities to determine the proportion which a uniform addition of glue would raise the critical concentration of each impurity. It is quite

certain that colloid additions quiet the gas action at both anode and cathode and thus lower the lead content of cathode zinc by preventing to a considerable extent the transportation of lead particles from the anode. Such additions also have an effect on the structure of the zinc deposit, tending to make it less crystalline. If carried to excess they will cause spongy deposits. The proper amount of such additions seems to be chiefly a factor of current density.

While full detail is not given for the results obtained for each impurity, all that was intended by this series of tests was to show the limiting values for each impurity under the conditions as outlined. All operations were conducted comparably to careful commercial practice, and a sufficient number of tests were made with each impurity to eliminate errors due to possible variations in other conditions than the direct effect of the single impurity being tested.

Of course, a large amount of very interesting experimentation could be developed from each separate case, by further varying the different conditions, but the results obtained for the single impurities mentioned appear very definite under the conditions as stated.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 21, 1922, President Schlueder-berg in the Chair.

THE EFFECT OF IMPURITIES IN NICKEL SALTS USED FOR ELECTRODEPOSITION.[1]

By M. R. Thompson and C. T. Thomas[2]

Abstract.

Experiments were conducted to determine the effect of the principal impurities present in nickel salts upon the character of the deposited nickel. It was found that of the impurities likely to be present copper and zinc are especially objectionable. Analyses were made of a considerable number of samples of commercial salts. Specifications for the purity of these materials are suggested.

I. INTRODUCTION.

During recent years the Bureau of Standards has received numerous inquiries from government departments and from commercial firms regarding the effect of various impurities in the baths used for nickel deposition and the amounts of such impurities that may be permissible in commercial nickel salts. A number of samples of these salts have been analyzed, from the results of which work it is apparent that there is at present a very great variation in the purity of these materials. It is recognized that it may not be feasible in all cases to attain a very high degree of purity without a prohibitive increase in cost. As, however, it has been found practicable by certain manufacturers to produce commercially materials which are nearly free from contamination, it seems desirable to suggest tentative limiting values for the probable impurities so that at least the grossly impure products may be excluded from the electroplating industry.

It is recognized that the conditions of operation in electroplating

[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce. Manuscript received August 16, 1922

[2] Chemist and Assistant Chemist, Bureau of Standards, Washington, D. C.

and electrotyping plants are so varied that it is likely that any conclusions reached from a limited number of small scale experiments may require some modification when applied to commercial practice. The conclusions and recommendations of this paper are presented, not with a view toward the establishing at this time of any "standard" specification for nickel salts, but rather for the purpose of establishing a basis of discussion among manufacturers and users of these materials and fostering their cooperation in the maintenance of high commercial quality. It is fully expected that the results here presented will require occasional revision as information upon the subject becomes more extensive. The tests described in this paper are largely empirical and no effort is made to consider fully the literature or theoretical considerations involved.

II. GENERAL CONSIDERATIONS.

Any specifications for the purity of nickel salts must take into account: (a) the sources and methods of manufacture of the salts, (b) the impurities likely to be present in them and the ease with which they can be removed, (c) the amounts of such impurities which are likely to be deleterious in the operation of the baths, and (d) the probability that appreciable amounts of these impurities may be introduced into the baths from sources other than the salts.

The principal nickel salts used in electrodeposition are nickel sulphate, the so-called "single salt", and nickel-ammonium sulphate, or "double salt." Nickel sulphate is produced by nickel refineries and as a by-product from copper refineries. In the former case the principal purification is accomplished in the refining of the nickel, which is subsequently dissolved in sulphuric acid. In the latter case the nickel sulphate is recovered from the contaminated liquors periodically removed from the copper refining baths. The preparation of a high grade nickel salt as a by-product of copper refining involves a considerable number of steps, the details of which may vary somewhat in different plants. Failure to use proper methods of purification has in certain cases caused the by-product salts to fall into disrepute. Certain manufacturers have, however, shown that it is entirely practicable to purify the by-product salts so that they are at least equal in quality to those

produced directly from metallic nickel. The source of the nickel salts is, therefore, not a criterion of their purity.

Nickel-ammonium sulphate is usually produced by crystallization after the addition of a calculated amount of ammonium sulphate to nickel sulphate solutions, such as the mother liquors from the crystallization of pure nickel sulphate. Owing to the relatively low solubility of double salt this operation affords a convenient means of recovering a large part of the nickel from mother liquors. The nickel-ammonium sulphate thus prepared is probably purer than the nickel sulphate solution from which it was precipitated, but may not be as pure as the crops of nickel sulphate preceding it. Actually, it is found in practice that there is no marked difference in the purity of these two commercial salts.

Analyses of a number of samples of salts believed to be typical of those now furnished commercially indicate that the principal harmful impurities likely to be present are copper, iron, zinc and free sulphuric acid. Usually only small amounts of insoluble matter are present and generally these are harmless materials, such as particles of wood, paper, etc., derived from containers. In no case has any appreciable amount of arsenic been detected in the salts examined by us. Nickel salts often contain a very small amount of chloride. In itself, this will usually be unimportant, since the formulas for most plating baths call for the addition of large amounts of chloride. It has also been found that appreciable amounts of magnesium sulphate may sometimes be present. One lot of nickel which was otherwise almost perfectly pure, contained over four percent of magnesium sulphate. This salt is not known to have any deleterious effects in the nickel bath and, in fact, it is sometimes purposely added to increase conductivity. It should preferably be absent from nickel salts on account of decreasing the nickel content of the latter by its presence. Nickel and cobalt are closely associated and most samples of nickel salts may be expected to contain a small amount of cobalt sulphate. Since the properties of these two metals are very similar, it is common practice to include the cobalt as nickel when determining the latter. Both metals are probably deposited in the plating bath in the same proportion that they deposit during an electrolytic analysis of the salt. No information is available as to whether

a small content of cobalt improves or injures the quality of a nickel deposit. Other impurities have not been considered in the present investigation.

III. METHODS OF EXPERIMENT.

The principal tests described in this paper were made by adding specified amounts of the designated metals (in the form of sulphates) to nickel baths made from salts which were shown by a careful test to be practically free from these impurities. The salts contained a small amount of magnesium sulphate, but it is believed that this substance could not have had any effect upon the results. All the tests were conducted in solutions of the following composition:

	g./L.	oz./gal.
Nickel sulphate (7 H_2O) *N*.....	140	19
Ammonium chloride 0.25 *N*.....	14	2
Boric acid 0.25 *M*.....	16	2

This solution, while by no means "standard", is believed to be typical of most of the solutions now used in electroplating. Deposits were made in the pure solutions and also in those containing definite amounts of impurities (a separate lot of solution being used in each case), for specified periods upon brass cathodes at a current density of 1 amp./dm^2 (9.3 amp./sq. ft). The acidity of the solutions was controlled by means of colorimetric measurements with appropriate indicators. The commercial 95-97 percent nickel anodes were employed. The character of the deposits was determined principally by visual observation, supplemented in some cases by the microscope.

IV. EFFECT OF ZINC.

The experiments upon the effect of zinc are summarized in Table I.

Several runs of from 1 to 42 hours duration were made in the case of each solution listed. The concentrations noted were those at the beginning of the series of experiments; no doubt this concentration decreased somewhat during the runs. In general, it

was observed that deposits made in later runs were decidedly superior to those immediately after the addition of the zinc sulphate. From these experiments the following conclusions were drawn.

1. Small amounts of zinc tend to cause bright edges and smooth surfaces. Larger amounts will bring out bright lines, spots and patches on the surface, and tend to increase pitting, the pits being separate from the bright spots, however. Excessive

TABLE I.

Effect of Zinc upon Nickel Deposits.

Percent Zn in Nickel Sulphate	Concentration of Zn^{--} in *N*-Ni Solution		Range of pH	Remarks
	g./L.	*N*		
0.03	0.04	0.001	5.0	Deposits satisfactory.
0.09	0.13	0.004	4.7–6.3	Deposits satisfactory. No certain effect of Zn noted.
0.20	0.28	0.009	5.1–6.4	Possible tendency toward bright edges and pitting, but rather good deposits on the whole.
0.30	0.42	0.013	4.9–5.5	Distinct tendency toward bright edges, bright splotches on surface and pitting. Deposit very smooth; little, if any, gassing.
0.44	0.62	0.019	4.7–6.6	Strong gassing from the start of deposition. Deposits loose, black and scaly from the start.

amounts of zinc will cause gassing at the cathode, attended by a very characteristic loose, black, scaly deposit, which is apparent from the start of deposition.

2. The effect of small or moderate amounts of zinc becomes more noticeable as the time of deposition is continued, from 1 to 10 or 12 hours sometimes being required to establish structures distinctly definite to the eye. Nevertheless, the influence is probably felt from the start and the accentuation is due to the gradual increase in the concentration of zinc ions around the cathode, caused by migration.

3. The permissible amount of zinc to be allowed in nickel sulphate, where thin deposits are concerned, would be about 0.2 percent; for thick deposits, 0.1 percent. This would correspond to about 0.3 and 0.15 g./L. respectively, in a normal nickel solution and would not furnish any margin of safety, nor allow for any accumulation of zinc from additions of nickel sulphate. (Zinc deposits after nickel according to the electrochemical series and hence may accumulate in a nickel solution). To allow for such possible accumulation and the resultant delayed effects, it would be safer to limit the amount of zinc in salts to 0.05 percent in the case of thin deposits (less than 1 hour) and to 0.03 percent in the case of thick deposits (24 hours). This specification should be readily met by most manufacturers.

4. Small variations of pH do not have much effect upon the action of zinc, but, by suitable adjustment of the pH, it has been found possible to prevent entirely the action of even excessive amounts of zinc. If the solution is neutralized with nickel hydroxide or carbonate to pH 6.7, allowed to settle, then filtered and re-acidified to say, pH 5.8, and electrolyzed at a high current density for some hours, a satisfactory deposit will be obtained and no further trouble experienced. Evidently, the zinc in solution is almost entirely precipitated at pH 6.7 and does not tend to re-dissolve rapidly. Filtration, or decantation, after neutralization is, therefore, not entirely necessary, but it would be very desirable to carry it out as an added precaution whenever the facilities are available.

V. EFFECT OF COPPER.

The experiments with copper are summarized in Table II.

Several runs, usually of from 18 to 24 hours duration, were made in the case of each solution listed. The concentrations stated were those present at the beginning of a series of experiments. As copper deposits more readily than nickel, the concentrations present in succeeding runs must have been appreciably less than those in the first runs. The amounts stated in the table may therefore be considered the maximum amounts present in these experiments. In all cases, it was found that the deposits in the later runs were of better quality than the initial deposits. From these experiments the following conclusions were drawn.

1. Small amounts of copper tend to cause a slight roughness near the bottom of a cathode, caused by scattered dark trees or "burrs." Larger amounts cause this roughness to spread up toward the top of the cathode. Excessive amounts cause, in addition, a very spongy, dark-gray voluminous deposit at the bottom. There seems to be no especial tendency toward gassing. The structures are quite characteristic.

TABLE II.

Effect of Copper upon Nickel Deposits.

Percent Cu in Nickel Sulphate	Concentration of Cu in *N*-Ni Solution		Range of pH	Remarks
	g./L.	*N*		
0.005	0.007	0.0002	5.15–5.85	Deposits satisfactory.
0.025	0.035	0.0011	5.15–5.75	Deposits satisfactory. No definite effect of Cu noted.
0.050	0.070	0.0022	5.15–5.80	A few small dark "burrs," or trees, near bottom edges.
0.100	0.140	0.0044	3.65–6.70	"Burred" all over, with dark gray spongy deposits at bottom.
0.500	0.700	0.022	5.10–6.45	Deposits as above, but much more exaggerated.

The reason why these growths predominate near the bottom probably lies in the fact that the convection currents in the solution near the cathode ascend vertically across the face and thus continually bring a fresh supply of copper ions to the vicinity of the bottom edge. As the stream rises, it becomes depleted in copper content and hence the upper portion of the cathode surface does not receive as great a supply of copper from this source. Migration of copper ions occurs, of course, more or less toward all portions of the surface, but migration is a slow process.

2. As with zinc, the effect of small or moderate amounts of copper seems to be greater the longer deposition is continued. In making a heavy nickel deposit, therefore, if the deposit is good at the start, it may still become bad after a few hours of deposition.

If the concentration of copper is great enough, however, a deposit will be bad from the very start.

3. The permissible amount of copper to be allowed in nickel salts, where thin deposits (less than 1 hour) are concerned, would be about 0.03 percent; for thick deposits (24 hours), 0.02 percent. This would correspond to about 0.04 and 0.03 g/L. respectively, in a normal nickel solution and would not furnish a margin of safety nor allow for any accumulation of copper from additions of nickel salts or from incomplete rinsing of articles previously copper plated. (Accumulation is less probable than with zinc because copper tends to become depleted in a nickel solution by electrolysis.) To allow for possible accumulation and the resultant effects, it would be safer to limit the amount of copper in salts to 0.02 percent in the case of thin deposits (less than 1 hour) and to 0.01 percent in the case of thick deposits (24 hours).

All commercial nickel anodes contain appreciable amounts of copper, usually from 0.10 to 0.25 percent. In view of this fact, it might at first appear unwarranted to restrict the copper content of the salts to 0.02 percent. If the copper and nickel from the anodes dissolved in the same proportion in which they are present there would be no advantage in attempting to exclude copper from the salts. It has been found, however, that under normal conditions of operation such as are used in nickel plating, most of the copper in the anodes remains in the anode slime and only a small proportion passes into the solution. Of the copper which is present in the solution (from any source), a portion is precipitated upon the nickel anodes during the time when no current is passing. Experiments have shown, however, that when the baths are again operated, most of this "cement copper" redissolves from the anodes and may be deposited upon the cathodes. As the nickel content of nickel sulphate is about 20 percent, 0.02 percent of copper in the nickel salts is equivalent to approximately 0.10 percent copper in the nickel anodes, which is probably as high a proportion as dissolves from the anodes under favorable operating conditions. It is not likely, therefore, that the copper content of the solution will become markedly affected by the solution of copper from the anodes.

4. As with zinc, small variations of pH do not seem to have much effect upon the action of copper, but the same method of

elimination by neutralizing and re-acidifying will completely remove the copper and result in obtaining good deposits where they were bad before. In the experiments performed the change was brought about more rapidly than with zinc. After a few hours, however, there seemed to be a tendency toward bad deposits again and a second treatment became necessary. Apparently, copper is less completely precipitated than zinc by the treatment, or else it re-dissolves more readily. Filtration is, therefore, all the more desirable.

It is common practice to purify a bath which has been found to be contaminated with copper by making the bath slightly acid and hanging scrap iron (or nickel) in the tank and thus removing the copper by a cementing action. The same result is secured by cleaning the anodes and allowing the copper to precipitate upon them while no current is passing. From the above discussion it is obvious that, if this method is used, the anodes should be cleaned again before further deposition. The cementation method is in some respects more convenient than the neutralization with nickel carbonate, etc. The latter method has the advantage, however, of removing any zinc that may possibly be present and perhaps certain other impurities less frequently encountered, such as arsenic. It will also remove all ferric iron present in solution (as previously pointed out by several observers) and has been found to remove a part of the ferrous iron.

Altogether, copper is certainly a more troublesome impurity than zinc and distinctly less of it can be tolerated with safety.

The Combined Effect of Zinc and Copper.

Since, as above noted, zinc tends to produce bright and smooth deposits and copper to produce dark and rough deposits, it is at least possible that under certain conditions these two metals may tend to counteract each other. In order to test this point a few runs were made in which definite amounts of these two elements were added to the nickel solutions. These experiments showed that, unless the concentration of zinc is very much in excess of that of the copper, the deleterious effect of the copper is still marked. In certain cases it was observed that when large amounts of zinc were added the deposits were improved. This observation is not reported with the view toward suggesting the addition of

zinc salts to nickel solutions containing copper, or *vice versa,* as this would be a very doubtful and unreliable expedient. The observation is of interest, however, in explaining apparent anomalies that have been or may be observed in determining the effect of zinc or copper compounds in nickel solutions.

VI. IRON.

The literature upon the effect of iron on nickel deposition is quite extensive, but unfortunately it contains many contradictory statements. Most of the European writers have condemned iron as very objectionable in nickel baths and have ascribed many of the defects of nickel plating, especially curling and cracking, to the presence of iron. They usually advise a periodical removal of iron from the bath. All the 95-97 percent nickel anodes used in this country contain appreciable amounts of iron, usually from 0.5 to 1.5 percent, and the 92 percent anodes, such as are still used by many platers, contain as much as 5 or 6 percent of iron. Under most conditions of operation, it is probable that practically all of the iron present in the anode is attacked during electrolysis and may pass into solution, although it may be subsequently reprecipitated wholly or in part, depending upon the conditions existing in the solution. The study of the effects of iron in nickel deposition is complicated by the fact that the iron exists in two states of oxidation and that ferrous and ferric hydroxide (or the corresponding basic salts) are precipitated at different degrees of acidity.

Further uncertainty is involved because of the tendency, especially of the ferric hydroxide, to exist in colloidal condition. It is believed that many of the apparent anomalies in the literature on the effect of iron in nickel deposition can be removed only by a thorough study of the effect of the hydrogen ion concentration, temperature and oxidation conditions upon the oxidation, hydrolysis and precipitation of ferrous and ferric hydroxides. We hope in the near future to conduct such an investigation. In so far, however, as specifications for nickel salts are concerned, the results of any such study are not of immediate interest. It can be readily shown that (a) all the nickel anodes now used commercially contain appreciable amounts of iron, (b) that the nickel plating baths contain in solution at all times as much iron as can be dissolved under the operating conditions employed and

(c) that the nickel deposits often contain appreciable amounts of iron. In view of these conditions, it is obviously not justifiable to attempt to exclude iron entirely from nickel salts. As all nickel anodes so far tested contained at least 0.5 percent of iron, which corresponds to 0.1 percent iron in the nickel salts, it is believed that the latter content is a reasonable requirement of purity for the salts. Not until it has been found practicable to obtain and apply nickel anodes containing much smaller amounts of iron than 0.5 percent, is any more rigid specification of iron content of nickel salts warranted.

A few preliminary experiments with the above nickel solution containing definite additions of ferrous sulphate lead to the following tentative conclusions:

1. It is possible to produce heavy nickel deposits containing from 2 to 7 percent of iron with no tendency whatever toward curling or cracking, provided the pH of the solution is regulated within certain limits.

2. The presence of iron in deposited nickel tends to make the latter distinctly whiter and more finely crystalline (therefore probably harder) than nickel nearly free from iron deposited at the same pH. This indicates a primary effect of iron on the internal structure of nickel deposits similar to that of variations of hydrogen ion concentration.[3]

3. There are some indications that ferric hydroxide in suspension may tend to cause increased porosity, especially upon those portions of the cathode which are inclined from the vertical and upon which suspended matter has a tendency to settle.

4. It is not possible, with the present limited knowledge, to state categorically whether the presence of iron in the nickel deposit is advantageous or objectionable. Even when more exact knowledge of the effects of iron is obtained, the purpose for which the deposits are made must be taken into account.

VII. FREE SULPHURIC ACID.

In a recent paper by one of the authors[4], the effects of acidity upon nickel deposition have been discussed in some detail. From

[3] M. R. Thompson, "Acidity of Nickel Depositing Solutions," Trans. Am. Electrochem. Soc., 1922, **41**, 233.

[4] M. R. Thompson, *loc. cit.*

the experiments there described it is apparent that the degree of acidity, or pH, is usually more significant than the exact amount of free acid present. With a given addition of free acid the change in pH produced will be determined approximately by the composition and buffer characteristics of the solution. As most of the nickel baths in commercial use contain boric acid, it is obvious that small amounts of free acid, such as may be present in nickel salts, are not likely to be very deleterious in themselves. The largest amount of free acid found in any of the commercial nickel salts was 0.21 percent and most of the samples contained less than 0.05 percent. It is significant that the sample containing a large amount of free acid was also badly contaminated with copper and zinc, which would indicate that the presence of much free acid may be a sign of careless or insufficient purification. One practical objection to the presence of much free acid in nickel salts is the fact that it may attack the paper or wood of the containers, thereby producing soluble organic impurities which may be deleterious in the baths. From practical considerations it is believed that a maximum of 0.10 percent of free sulphuric acid is a reasonable specification.

VIII. ANALYSIS OF COMMERCIAL NICKEL SALTS.

In Tables III and IV is found a summary of analyses of typical commercial samples, most of which were those furnished to one of the Government departments in connection with bids or deliveries.

Methods of Analysis.

In applying the methods of analysis, no attempt was made to attain the highest degree of refinement. It is believed, however, that with large samples under the conditions stated, the results are certainly accurate to 0.01 percent of each constituent and probably to 0.005 percent. Where blank spaces appear in Tables III and IV, the content of impurity was estimated to be less than 0.005 percent and, therefore, probably not significant.

A 25 g. sample of the salt is dissolved in water and diluted to 250 cc. Fifty cubic centimeters (equivalent to 5 g.) is used for the determination of free acid and iron. The remaining 200 cc. (equivalent to 20 g.) is used for the determination of copper and zinc.

Free Acid. A few drops of methyl red soution are added to 50 cc. of the solution and 0.1 *N* sodium hydroxide is added, while shaking, until the dark color disappears and a greenish yellow color

TABLE III.

Analyses of Commercial Nickel Sulphate.

Sample No.	Zinc Percent	Copper Percent	Iron Percent	Free Acid Percent
1	....	0.011	....	....
2*	....	0.039*	....	....
3*	....	0.005	0.130*	0.020
4	....	....	0.045	0.015
5*	0.120*	0.050*	0.020	0.210*
6	0.044	0.014	0.040	0.040
7	....	0.018	0.100	0.025
8*	0.088*	0.010	0.110*	0.075
9†	0.010	0.016	0.100	....
10*	0.016	0.024*	0.070	....
11*	0.010	0.034*	....	....
12*	0.010	....	0.120*	....
13	....	0.005	....	....
Average:	0.022	0.017	0.057	0.030

* Samples marked * would be rejected by the specification proposed in Table V.
† Samples 9 to 12, inclusive, are from four different barrels of the same shipment.

TABLE IV.

Analyses of Commercial Nickel-Ammonium Sulphate.

Sample No.	Zinc Percent	Copper Percent	Iron Percent	Free Acid Percent
1*	....	0.045*	....	....
2*	....	0.058*	0.025	0.030
3	....	....	....	....
4*	0.028	0.050*	0.035	0.070
5	0.010	0.017	0.024	0.070
Average:	0.008	0.034	0.017	0.034

* Samples marked * would be rejected by the specification proposed in Table V.

is produced without the presence of any permanent precipitate. The suggested limit of 0.1 percent free H_2SO_4 is equivalent to 1 cc. of 0.1 *N* NaOH on a 5 g. sample. The titration of total acidity is stopped at an end point corresponding to between pH 5.5 and 6.0.

Iron. After the above described titration, the solution is boiled with two drops of nitric acid to oxidize the iron, which is then precipitated with an excess of ammonia. Ferric hydroxide is filtered out, washed with hot water, dissolved in hydrochloric acid and reprecipitated with ammonia. It is then ignited and weighed as Fe_2O_3. If alumina is suspected to be present the precipitate may be dissolved and iron determined volumetrically.

Copper. A 200 cc. portion is acidified by the addition of 10 cc. of concentrated sulphuric acid. The copper is obtained by electrolysis with a rotating platinum anode and platinum cathode. Unless present in excessive amount the copper is completely precipitated in thirty minutes, using a current of about 2 amperes (a cathode current density from 2 to 3 amp./dm.^{2}.).

Zinc. The filtrate from the copper is made slightly alkaline with ammonia and a solution of citric acid is added until the solution is acid to methyl red, corresponding to a pH of 4.0 to 5.0. A rapid stream of hydrogen sulphide is then run into the cold solution for fifteen minutes, the zinc being completely precipitated. The precipitate of zinc sulphide usually has a dark color, indicating the presence of a small amount of nickel sulphide. Unless perfectly white the zinc sulphide is filtered out, dissolved in dilute sulphuric acid and reprecipitated as above. The precipitate obtained at room temperature is more easily filterable than that from a warm solution. In any case, a close grained filter paper is necessary. The zinc sulphide is washed, ignited and weighed as ZnO.

IX. TENTATIVE SPECIFICATIONS.

It is believed that the analyses of the commercial nickel salts show that it is entirely practicable to furnish nickel salts with less than the maximum content of impurities shown in Table V. From Tables III and IV it appears that about one-half the samples tested would meet these requirements.

Strictly speaking, a more rigid specification is justified for nickel-ammonium sulphate than for nickel sulphate, owing to the fact that the former contains only about two-thirds as much nickel as the latter, and the ratio of nickel to the impurities is probably the determining factor. As, however, the nickel-ammonium sulphate is not now as extensively used as the nickel sulphate, and

as its concentration in the baths is limited by its comparatively low solubility, it is suggested that for practical purposes the same specification may be applied to both salts.

It will be observed that, when calculated in terms of the constituents probably present in the salts, the amount of impurities allowed is by no means negligible, in fact it becomes a total of 0.9 percent. This is equivalent to a requirement of 99.1 percent of the pure salt without considering any other impurities than those mentioned. This latter requirement cannot, however, be defined

TABLE V.

Proposed Specifications for Nickel Salts.

Not over	Percent	Calculated as	Percent
Zinc	0.05	$ZnSO_4.7H_2O$	0.22
Copper	0.02	$CuSO_4.5H_2O$	0.08
Iron	0.10	$FeSO_4.7H_2O$	0.50
Free acid	0.10	H_2SO_4	0.10
			0.90
Nickel in Single Salts:			
Not less than 21.39 percent ($NiSO_4$ with "$6.5H_2O$.")			99.10
			100.00
Nickel in Double Salts:			
Not less than 14.72 percent ($NiSO_4(NH_4)_2SO_4.6H_2O$)			99.10
Impurities (as above)			0.90
			100.00

for nickel sulphate in terms of the nickel content, owing to the fact that nickel sulphate as now made may contain crystals with six or with seven molecules of water, depending upon the conditions of crystallization. If, as seems probable, both of these compounds are present in the commercial product, we may arbitrarily assume the formula $NiSO_4.6.5H_2O$ to represent average conditions. On this basis, the nickel content of the pure single salt would be 21.6 percent and that of the 99.1 percent salt would be 21.4 percent. The double salt is probably $NiSO_4\ (NH_4)_2SO_4.6H_2O$, containing 14.9 percent nickel when pure, or 14.7 percent when 99.1 percent pure. Owing to the possibility of efflorescence of the double salt and to uncertainty in the composition of the single salt, it should be emphasized that the

specification of the nickel content is no criterion of the purity of the salts and is useful only in assuring that a definite amount of nickel is obtained.[5]

X. CONCLUSION.

It is believed that, if the above specifications are found to be consistent with the experience of those engaged in nickel deposition, there will be no serious difficulty in getting the co-operation of manufacturers in producing salts of the desired purity. In connection with the furnishing of samples of salts to be analyzed, several manufacturers have assured this Bureau of their willingness to assist in maintaining a high standard of purity for these materials. The authors wish to acknowledge the courtesy of numerous firms in furnishing samples and information regarding their products, and to express their appreciation for the assistance of Mr. J. H. Winkler in preparing the electrolytic deposits, and for suggestions and advice from Dr. William Blum, under whose direction this investigation was conducted. Valuable suggestions were also received from Mr. G. B. Hogaboom, Electroplating Adviser to the Bureau of Standards and from the Research Committee of the American Electroplaters' Society.

DISCUSSION.

COLIN G. FINK[1]: Has any account been taken of the organic impurities in these nickel salts? I know that nickel salts which have been exposed to organic dust are not as serviceable in good plating practice as salts which have been carefully kept out of contact with organic materials and dust, and sealed in glass bottles.

WILLIAM BLUM[2]: I can confirm all that Dr. Fink says about the effect of small amounts of organic matter on nickel deposition.

[5] The theoretical nickel content of pure salts is as follows:

$NiSO_4 \cdot 6H_2O$	22.33 Percent
$NiSO_4 \cdot 7H_2O$	20.89 Percent
$NiSO_4 (NH_4)_2 SO_4 \cdot 6H_2O$	14.86 Percent

[1] Consulting Electrometallurgist, New York City.

[2] Chemist, Bureau of Standards, Washington, D. C.

We know of cases in which a nickel solution was entirely ruined from the small amount of dextrin taken up by filtering through new muslin.

Reference is made in the paper to an otherwise high grade of salt containing four percent of magnesium sulphate. This was probably introduced in the operation of removing the other impurities, due to the use of lime which was high in magnesia.

R. J. McKay[3]: The last discussion of Dr. Blum brings up an interesting point. I believe it would be better to make the specifications for nickel salts according to the effect of the various impurities on plating, rather than according to the analysis of the present commercial salts on the market.

It is suggested that we take an average analysis of the salts and use it for a specification. If we take the average of the present variation and say, "We must always be better than this average," that means that the price of the salts must go up in order to increase the purity, because the average, after adopting this specification, must be better than the present average.

William Blum: You will note that this paper deals with nickel salts for use for electrodeposition. A large amount of a badly contaminated nickel sulphate was purchased by one of the Government departments. Upon inquiry, the manufacturer stated that it was never intended for electrodeposition—it was intended for soap manufacturers, and they were sorry it got into the hands of electroplaters. It may therefore be necessary and desirable to go to more trouble or expense to make a high grade nickel salt to be used for electrodeposition, and to use those materials which are not susceptible to purification for other purposes, in which the particular impurities are less deleterious.

Wilder D. Bancroft[4]: I want to ask Dr. Blum whether it might not be the case that some of the magnesium precipitated with the nickel. I know it was shown in Germany, a good many years ago, that a mixture of magnesium sulphate and nickel sulphate precipitates magnesium along with the nickel, but I do not know whether they did it in concentrations of the order that you are actually using. If some of the magnesium comes down with

[3] International Nickel Co., New York City.

[4] Professor of Physical Chemistry, Cornell Univ. Ithaca, N. Y.

the nickel it might well account for a beneficial or harmful deposit, as you please.

WILLIAM BLUM: We know that there may be traces of magnesium in electrodeposited nickel, but we have not been able to learn whether it is there as an alloy as suggested, or whether it is there as a hydroxide. We hope to study this subject.

W. E. HUGHES[5] (*Communicated*): In my opinion, a copy of Messrs. Thompson and Thomas' paper ought to be in the hands of every nickel plater and every buyer of nickel salts. My experience of twenty years in workshop and laboratory enables me to confirm most of the observations made by the authors. But, at the same time, my experience (sometimes bitter) causes me to differ from them on one matter. No content of copper, zinc, or acid, ought to be allowed in the purchase specifications of nickel salts. Salts have been marketed for years—and at competitive prices—that contain no percentage of copper and zinc that can be recognized by known methods of chemical analysis; and the amount of hydrogen ions present is not more than can be accounted for by hydrolysis. Tons of nickel salts complying with the requisites indicated have passed through my hands. It was my rule that every batch of salts entering the works should be examined by two chemists, working independently, for traces of copper and zinc. There was trouble at first with the makers, who complained that my standards could not be satisfied by a commercial competitive product. However, when they found they had to satisfy them, or lose orders, they found means to do so; and for years I never passed a batch of salts for factory use that did not comply with my specification.

In regard to acid content, I suggest that small crystal stuff should be specified. I do not mean crushed material, but the small crystal product of rapid crystallization from hot, saturated solutions. Such stuff is much less liable to contain or be contaminated with mother liquor. It is clean, easy to handle, and easy to dissolve or to mix with other components of nickel baths. It is a commercial product, and it is on the market at competitive prices.

I agree with the authors that a small amount of iron will do

[5] Electrometallurgist, Seaford, Sussex, England.

no harm in a nickel bath. This is clear from practical experience, for, if it were harmful no nickel bath would run a month under ordinary workshop conditions. Magnesium is, as I have found, an excellent component for a single salt nickel bath to contain. All the same, it should be absent from nickel salts as purchased. The plater pays for nickel salts, not for medicine.

M. R. THOMPSON (*Communicated*): Referring to Dr. McKay's discussion, the specification suggested in Table V is based upon both the analysis of commercial salts as given in Tables III and IV, and also the experimental effect of zinc and copper upon deposits as given in Tables I and II. It seemed desirable to consider the matter from both standpoints until further data are obtainable.

As a matter of fact, the specification suggested is actually less rigid than the a v e r a g e of any impurity found in either single or double salts, with the exception of the average copper content of double salts. This condition, coupled with the fact that several manufacturers are already supplying salts practically free from all harmful impurities, ought to exclude the question of increased cost if the specification is adopted. It is not so much a question of increasing the a v e r a g e purity of the salts obtainable at present, as it is of eliminating all salts below an acceptable standard of purity; not requiring more but better work during manufacture.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 21, 1922, President Schlueder-berg in the Chair.

THE APPLICATION OF CONTRACTOMETER TO THE STUDY OF NICKEL DEPOSITION.[1]

By E. A. Vuilleumier[2]

Abstract

When nickel is deposited on thin sheets of platinum the cathode bends toward the anode. This bending is measured by means of a contractometer.

I. INTRODUCTION.

The peeling of nickel deposits has been attributed to such factors as the presence of hydrogen, occluded, adsorbed, or alloyed; to over-voltage; to "reaction resistance"; to the presence of iron; to unfavorable pH; to high current density; and to unsatisfactory cleansing of the surface to be plated. The primary cause, however, seems to be a tendency of the nickel as deposited to undergo a spontaneous contraction. The degree of this contraction can be measured accurately and conveniently by means of the contractometer as developed by Kohlschütter and Vuilleumier.[3]

II. THE CONTRACTOMETER.

The contractometer blade is a piece of sheet platinum, 6 cm. by 2 cm. by 0.1 mm. A narrow platinum strip is welded to the center of the bottom of this foil. This strip is twisted around a light glass pointer, 30 cm. long. The side of the foil away from the pointer is insulated by painting with vaseline. A millimeter scale is attached and adjusted so that the end of the pointer can move along its length. (See Fig. 1). With the aid of a lens, readings can be made to tenths of millimeters. The foil is immersed 3 cm.; the area plated is therefore 6 sq. cm.

[1] Manuscript received August 19, 1922.
[2] Dickinson College, Carlisle, Pa.
[3] Zeitschr. f. Elektrochemie 1918, 24, 300.

When this platinum foil is made the cathode in a nickel bath and the circuit is closed, the pointer at once begins to move toward the r i g h t. When the current is broken the pointer ordinarily stands still at once. After each measurement the nickel is dissolved in warm concentrated nitric acid, the insulation is burned off, and the apparatus is ready for a new contractometric measurement.

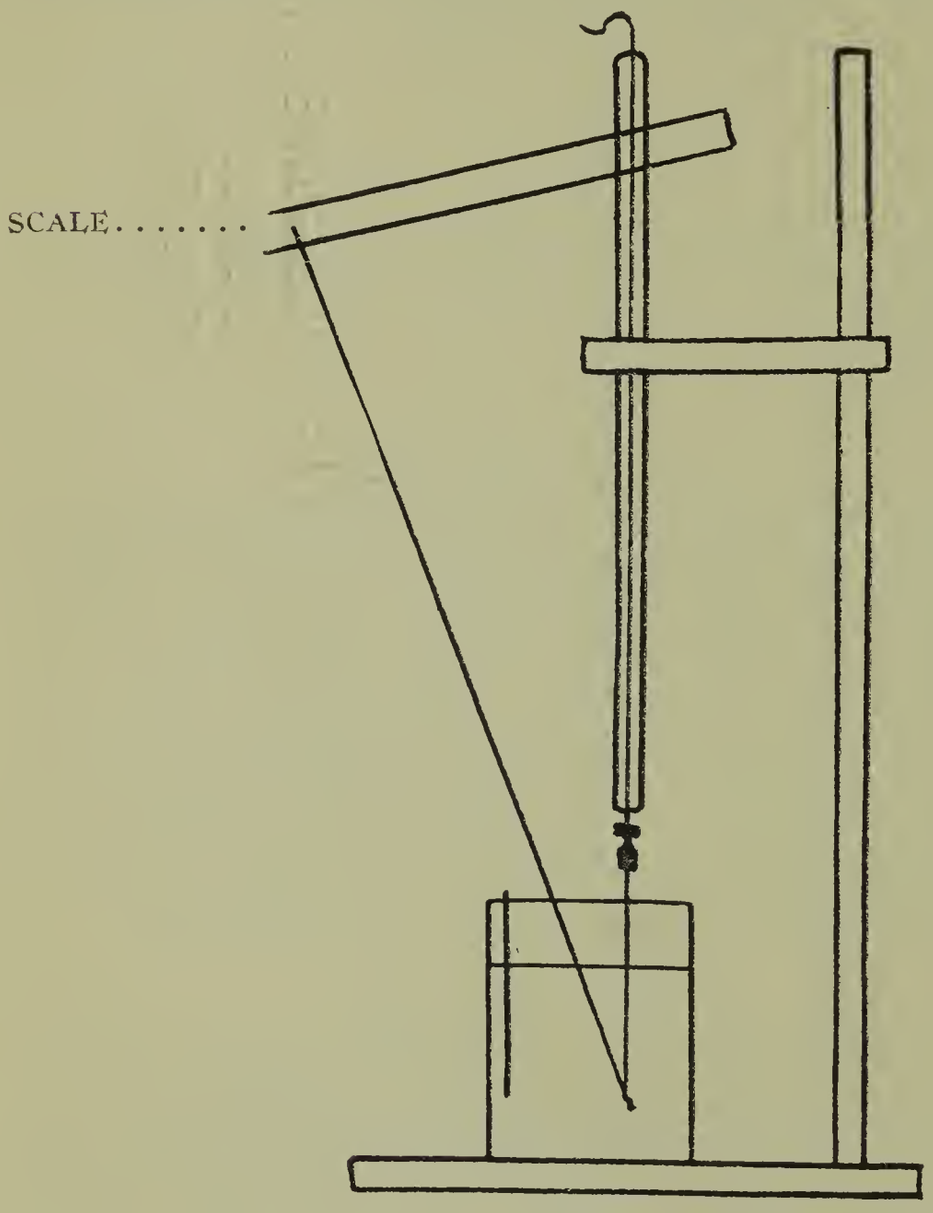


FIG. 1. The Contractometer

III. THE NICKEL SOLUTION.

A kilogram of nickel castings were dissolved in hydrochloric acid, chlorine water was added, and the solution was twice evaporated to dryness. The impure product was treated with an excess of freshly precipitated nickel carbonate and filtered. The

solution, which was 3*N* in nickel, was found to be free from iron, copper and zinc.

Electrolytes made from the new stock solution showed considerable variation in the contractometric readings; after ageing for several months, however, the results obtained were reproduceable. In the meanwhile a basic salt had been deposited on the walls of the container. The solution in equilibrium with this basic deposit was "very faintly acid" toward litmus.

A fresh portion of the stock solution was used for making up each separate electrolyte. The experiments recorded in this paper were conducted at a temperature of 16 to 18° C. The electrolyte was not agitated. The anode used was prepared electrolytically from the pure stock solution.

IV. REPRODUCIBILITY OF RESULTS.

The reproducibility of contractometric results is illustrated by results obtained under definite conditions. These are given in Tables I and II.

TABLE I.

Reproducibility of Results.

0.25 *N* $NiCl_2$ acidulated with acetic acid

(a) 0.17 *N* CH_3COOH; 0.3 amp./dm.^{2}

Deflection after 30 minutes, in mm.

10.8 10.7 9.6

(b) 0.17 *N* CH_3COOH; 0.6 amp./dm.^{2}

Deflection after 30 minutes, in mm.

15.3 16.5 16.9 16.2

(c) 0.20 *N* CH_3COOH; 0.5 amp./dm.^{2}

Deflections at 5-minute intervals.

Time Min.	Deflection mm.	Diff./5 Min.	Time Min.	Deflection mm.	Diff./5 Min.
0	0				
5	4.2	4.2	35	18.0	2.2
10	7.2	3.0	40	19.5	1.4
15	9.7	2.5	45	21.3	1.8
20	11.8	2.1	50	23.1	1.8
25	14.0	2.2	55	24.8	1.7
30	15.8	1.8	60	26.3	1.5

Table II.

Reproducibility of Results.

0.25 *N* $NiCl_2$ acidulated with hydrochloric acid.
0.02 *N* HCl 0.5 amp./dm.^{2}

	170		172		173		196	
Time Min.	Deflection mm.	Diff/5 Min.	Deflection mm.	Diff./5 Min.	Deflection mm.	Diff./5 Min.	Deflection mm.	Diff./5 Min.
0	0		0		0		0	
5	4.9	4.9	5.1	5.1	4.5	4.5	4.9	4.9
10	8.0	3.1	8.6	3.5	7.6	3.1	8.1	3.2
15	10.6	2.6	11.5	2.9	10.3	2.7	10.3	2.2

V. THE SLOWING UP OF THE POINTER. THE CONTRACTION OF COPPER, IRON AND SILVER.

Tables I and II also illustrate a slowing up of the pointer as nickel is deposited. At first sight it seemed that this slowing up of the pointer might be due to a decrease in the elasticity of the bent platinum. Upon closer examination it could be noted, however, that a change in the structure of the deposit always paralleled the slowing up.

This was brought out most clearly in the electrolysis of two copper solutions. Sieverts and Wippelman[4] have shown that an acidulated solution of copper sulphate gave a deposit that in its early stages was dense and smooth. As the electrolysis proceeded, however, the deposit became coarsely crystalline. On the other hand, an alkaline copper tartrate bath continued to give a dense and smooth deposit. The pointer moved uniformly in the latter solution; in the former, however, it quickly slowed up as the deposit became coarsely crystalline.

In the case of nickel the deposit in its early stages was dense and smooth; as the electrolysis progressed it was likewise observed that the deposit had a tendency to become coarsely crystalline. Silver deposited from a cyanide bath showed a slight contraction that likewise decreased as the deposit became coarse. In the case of iron the point actually moved faster as the electrolysis progressed. The results are recorded in Table III.

[4] Zeitschr f. anorg. Chemie, 1915, **91**, 1.

TABLE III.

Contraction of Copper, Iron and Silver.

30 g. $CuSo_4$; 150 g. Rochelle Salt; 48 g. NaOH per Liter. 1.0 amp./dm.^{2}			6.25 g. $CuSo_4$; 4 drops Conc. H_2SO_4 per 50 cc. 1.3 amp./dm.^{2}		
Time Min.	Deflection mm.	Diff./1 Min.	Time Min.	Deflection mm.	Diff./1 Min.
0	0		0	0	
1	0.6	0.6	1	0.5	0.5
2	1.2	0.6	2.5	0.9	0.16
3	1.7	0.5	5	1.2	0.12
4	2.3	0.6	10	1.7	0.10
10	6.2	0.65	15	2.1	0.08
15	8.3	0.6			
0.5 *N* $FeSO_4$ 0.5 amp./dm.^{2}			0.5 *N* $AgNO_3$; 2 *N* KCN 0.5 amp./dm.^{2}		
Time Min.	Deflection mm.	Diff./5 Min.	Time Min.	Deflection mm.	Diff./5 Min.
0	0		0	0	
5	3.5	3.5	5	1.0	1.0
10	8.1	4.6	10	1.4	0.4
15	13.7	5.6	15	1.7	0.3
20	20.5	6.8			

VI. EFFECT OF pH ON THE CONTRACTION

When the current was passed through a nickel solution that was "practically neutral", the pointer moved for a few minutes, then stood still. At the same time the deposit became black and green. When the solution was made "slightly acid" with acetic or hydrochloric acid, the pointer moved rapidly. A further increase in acidity slowed up the pointer, at the same time reducing the cathode efficiency. A series of experiments is planned in which the pH will be controlled according to the method recently applied by M. R. Thompson.[5]

VII. EFFECT OF FOREIGN METALS AND CONDUCTING SALTS.

The contractometer was very sensitive to the addition of various substances to the electrolyte. Thus it was noted that the addition of a small quantity of iron to an acid nickel bath caused an in-

[5] Trans. Am. Electrochem. Soc. 1922, **41**, 333.

crease in the deflection of almost fifty percent. A trace of zinc, on the other hand, caused a marked decrease in the deflection, the deposit becoming velvety. (See Table IV). Conducting salts gave

TABLE IV.

Effect of Foreign Metals and Conducting Salts on an Acid Electrolyte.

0.25 *N* $NiCl_2$; 0.02 *N* HCl
0.5 amp./dm.^{2}

No.	196		204 0.005 *N* $FeSO_4$		216 0.005 *N* $ZnSO_4$		230 *N* NaCl	
Time Min.	Deflection mm.	Diff./5 Min.	Deflection mm.	Diff./5 Min.	Deflection mm.	Diff./5 Min.	Deflection mm.	Diff./5 Min.
0	0		0		0		0	
5	5.3	5.3	5.2	5.2	1.0	1.0	9.1	9.1
10	9.0	3.7	10.8	5.6	1.9	0.9	15.2	6.1
15	11.0	2.9	16.0	5.2	3.0	1.1	20.5	5.3
20			21.5	5.5				
25			27.9	6.4				
30			34.5	6.6				

rise to black spots and stripes such as are noted when the acidity of a solution is too low.

An electrolyte containing ammonium chloride and free ammonia gave a deposit that was dark and velvety (See Table V).

TABLE V.

Effect of Zinc on an Alkaline Electrolyte.

0.25 *N* $NiCl_2$; *N* NH_4Cl; 0.25 *N* NH_3
0.5 amp./dm^2

No.	228		225 0.005 *N* $ZnSO_4$	
Time Min.	Deflection mm.	Diff./5 Min.	Deflection mm.	Diff./5 Min.
0	0		0	
5	10.4	10.4	12.2	12.2
10	18.5	8.1	24.8	12.6
15	25.0	7.0	37.7	12.5

The pointer moved fast, due in part, probably, to high current efficiency. The addition of a trace of zinc in this case gave rise to a bright deposit, associated with an even faster movement of the pointer.

Stäger[6] has studied the effect of depolarizers upon a $2N$-$NiCl_2$: N-NH_4Cl solution. Oxidizing agents such as hydrogen peroxide and potassium chlorate gave rise to low deflections; the current efficiency is so low, however, that it is difficult to draw definite conclusions from his observations. When he saturated the solution with sodium cinnamate, an unsaturated compound, he found that the deposit was crystalline, and that the pointer moved slowly.

TABLE VI.

Delays and Spurts in the Contraction.

No.	32 N $NiCl_2$; 0.08-M Boric Acid 0.5 amp./dm²		6 b N $NiCl_2$ N NH_4Cl 0.5 amp./dm²	
Time Min.	Deflection mm.	Diff./2 Min.	Deflection mm.	Diff./2 Min.
0	0		0	
2	7.5	4	13	13
4	13.5	6	23	10
6	18.5	5	34	11
8	23.5	5	59	25*
10	26.5	3	68	9
12	30.5	4	78	10
13	60.5			
14	87.5	57*		
15	91.5	2		

* Spurt.

VIII. DELAYS AND SPURTS IN THE CONTRACTION.

When solutions were used from which little or no hydrogen was liberated during the deposition, that is, solutions containing boric acid or ammonium chloride, the pointer at times showed a behavior that is illustrated by experiments 32 and 6b, Table VI. The pointer at first seemed to move normally, then took a rapid spurt and again moved normally. The spurt was especially common in numerous experiments involving a nickel chloride-ammonium chloride electrolyte.

[6] Helvetica Chimica Acta, 1920, 3, 584.

IX. INFLUENCE OF TEMPERATURE.

The influence of temperature is of importance because of its effect upon the cathode potential as well as upon the form of the nickel deposited. Matters are somewhat complicated by the fact that a change in temperature influences the nature of the electrolyte. Stäger[7] found that working at higher temperatures gave rise to crystalline deposits and a decrease in the deflection of the pointer. In a private communication M. R. Thompson states that this is probably due in part to increased metal ion concentration resulting from increased dissociation. The effect noted is in accordance with Bancroft's axiom.[8]

X. MAKING THE NICKELED CONTRACTOMETER THE ANODE.

When at the close of a measurement the current was reversed, thus dissolving the nickel, the pointer moved toward the left, and stopped at or near the original position.

XI. EFFECT OF HYDROGEN.

The nickeled contractometer was carefully rinsed, the electrolyte was replaced by dilute sulphuric acid, and the nickel anode was replaced by one of platinum. When hydrogen was liberated the pointer moved several centimeters toward the l e f t. When the current was broken the pointer flew back. Hydrogen therefore causes an e x p a n s i o n of nickel, possibly forming an alloy of the palladium-hydrogen type. It should be mentioned that hydrogen under these conditions had practically no effect on the unplated platinum contractometer.

XII. CATHODE POTENTIAL AND THE STRUCTURE OF NICKEL.

Stäger[9] has found that superimposing an alternating current gave rise to crystalline deposits and to a slow deflection. Kohlschütter and Schödl,[10] have found that superimposing an alternating current lowers the cathode potential.

XIII. OTHER APPLICATIONS OF THE CONTRACTOMETER.

Kohlschütter and Stäger[11] have used the contractometer as anode to study a variety of reactions in which the anode undergoes a change.

[7] Helvet. 1920, **3**, 384.
[8] Blum, Trans. Am. Electrochem. Soc., 1919, **36**, 213.
[9] Helvet. 1920 **3**, 584.
[10] Helvet. 1922, **5**, 490 and 593
[11] Helvet, 1921, **4**, 821.

When the contractometer was plantinized, it served to study oxygen polarization; when it was nickeled, to study the Edison cell reaction; when it was copper plated, to study the formation and nature of copper hydroxide; when it was iron plated, to study the formation of passive iron; when it was silver plated, to study the formation of silver sulphide. These applications suggest a large field of usefulness for the contractometer.

XIV. THE CONTRACTOMETER AND THE PEELING OF NICKEL DEPOSITS.

When nickel is deposited on thin sheets of metal, the nickel contracts and bends the cathode. When it is deposited on a rigid base it has a tendency to tear itself away from the cathode, in other words, to peel. Various solutions give deposits that show great differences in the degree of contraction. In general it was noticed that a solution that gave large contractometric readings also gave deposits showing a marked tendency to peel.

XV. SUMMARY.

1. The mechanical stresses of nickel as deposited were studied by plating the nickel on one side of a thin sheet of platinum and measuring the bending or contraction.

2. The degree of contraction decreases when the deposit becomes more coarsely crystalline.

3. There are at times delays and spurts in the contraction, especially when little or no hydrogen is liberated during the deposition.

4. Hydrogen, when and while electrolytically deposited, causes the nickel to expand.

5. The contraction of the nickel is evidently a function of the size of the crystalline grains, etc., and the consequent amount of internal stress in the deposit. There are a number of factors influencing the structure of the deposit, such as metal ion concentration, hydrogen ion concentration, current density, temperature, etc.

6. The contractometer is discussed in connection with the peeling deposits, and other applications to electrodeposition.

DISCUSSION.

WILLIAM BLUM[1]: There must be two conditions which determine the adhesion of a deposited metal. One is the tendency of the metal to contract or to pull away; the other is the tendency for it to adhere. The tendency to contract, measured by Dr. Vuilleumier, is not peculiar to nickel, although it is more marked with nickel than with any other metal. The tendency for it to adhere is essentially a function of the cleanness of the surface; in other words, of the intimacy of contact between the electrodeposited metal and the base metal.

At first sight the contraction may appear to be due to absorption of hydrogen in the nickel. The interesting thing is that if nickel is deposited and then hydrogen is liberated on it, the needle goes the other way. Therefore, the evolution of hydrogen at the cathode, and its possible absorption by the deposit, will not account for the contraction of nickel deposited from acid solutions. The character of the crystalline structure of the nickel so deposited probably accounts for its greater tendency to contract, rather than the occlusion or inclusion of hydrogen in any form.

There is a great need for a method of measuring adhesion of an electrodeposited metal to a base metal. The only experiments that I recall in that connection were made by Dr. C. F. Burgess, on the adhesion of electrodeposited and hot-dip zinc coatings. He soldered a piece of metal to the coating and determined the load required to detach the coating. It is at least possible that the physical properties or the adhesion were changed during the soldering operation.

W. D. BANCROFT[2]: There is another side of this question of contraction which interests me very much, although it does not come strictly under the heading of electrodeposition, and that is the contraction of porous metals, which we have to deal with in the case of contact catalysis.

We were doing some work this last year on the adsorption of hydrogen and carbon monoxide by platinum black, and we found it was absolutely impossible to get reproducible results, because

[1] Chemist, Bureau of Standards, Washington, D. C.
[2] Prof. of Physical Chem., Cornell University, Ithaca, N. Y.

if you heated the platinum black high enough so that you could pump out all the gas, the platinum black sintered together and its power of adsorption was changed absolutely. If, instead of doing that, you precipitate your platinum black on asbestos, under these circumstances, it apparently adheres to the asbestos with sufficient strength, so that you have an entirely reproducible material. You can heat that up and you can get results which you can duplicate.

There you have counteracted your effect of contraction by putting it not on a base metal, but on another base, and I have no doubt that the same thing occurs with nickel on pumice. My personal experience happens to have been with the platinum on asbestos.

The whole question of contraction is really a much larger one than the particular case that we happen to be dealing with here. I hope that it will be considered in all its bearings, and not merely in just one of them. I do not envy the man the job of doing quantitative work on the forces coming in, that cause contraction or sintering of porous metals, but it is really part of the same problem.

J. D. Alley[3]: We found in the electrodeposition of iron for building up worn parts, where one of the essential things is adhesion, that absolute cleanliness is essential. We tried quite a number of different methods of cleaning, and the only way we could get it to adhere at all was to use electrolytic cleaning. Of course, this is a case where you are depositing iron on iron. We used cold rolled steel rods and used three different tests for adhesion.

In the first test we plated the iron on the cold rolled rod, which was a half inch in diameter; then we would hold it in a vise, bend it to a right angle, bend it back, bend it back straight, and bend it in the opposite direction to a right angle, bend it back straight again, and the plated iron would adhere and not crack off.

In the second test we took a piece of cold rolled steel about an inch thick and had a hole drilled in it. We plated on our rods and ground them accurately to size; the hole in the cold rolled steel block was made a half mil smaller than the rods, and we pressed

[3] Wilkinsburg, Pa.

those rods through this hole and back, and there were no signs of stripping of the plated material from the parent metal.

In the third test we heated the iron after the material had been plated on, and forged it. We could not get it to crack or break off, and in the microphotographs of it that were taken, we could not see a dividing line between the plated-on material and the original cold rolled steel, except in the difference in the appearance of the two metals.

W. E. HUGHES[4] (*Communicated*): Dr. Vuilleumier's paper is of great interest. It is a continuation of the study of the phenomena occurring during the deposition of metals by a method originated by him and Professor Kohlschütter, and quite different from those adopted by Mills[5] and, independently, by Bouty[6], on the one hand, and, on the other hand and later, by Stoney[7].

An interesting observation is that hydrogen, when and while electrolytically deposited, caused the nickel to expand; but why this fact should indicate that an alloy is, possibly, formed is not at all clear. Nor can I see any evidence that "contraction is a function of the size of the crystalline grains, and the consequent amount of internal stress in the deposit." It does not at all follow that, because the slowing up of the movement of the pointer was concurrent with the deposit becoming more crystalline to the eye, increase in grain-size and contraction are functionally related. One has to consider what the movement of the pointer really indicates. It shows the bending of the cathode by the deposit indeed, but the cathode must be considered as a whole, namely, platinum plus nickel deposit.

Now, whereas the first-formed thin layer of deposited nickel causes the bending of the platinum, the layer next formed causes the bending of platinum p l u s first layer of nickel. Further movement of the pointer indicates bending of the platinum p l u s the first two layers of deposit; and so on. Will it not require more force for the second layer to produce its effect than the first, for the third than the second, and so on? Surely, this must be so, as Mills points out; and if it is, the slowing up of the movement

[4] Electrometallurgist, Seaford, Sussex, England.
[5] Proc. Roy. Soc. 1877, **26**, 504.
[6] *Compt. rend.* 1879, **88**, 714.
[7] Proc. Roy. Soc. 1909, **82**, 172.

of the pointer as deposition continues is accounted for, and easily, by dynamical considerations. There will come a time in the course of every instance of deposition when the force of bending is balanced by resistance to bending of the already deposited nickel.

Increase in grain-size need, therefore, have nothing to do with contraction. On the other hand, I have found, in cases of iron[8] and copper[9] deposition, that slip within the grains of a deposit occurs in the outer and larger grains of a thick deposit as plainly and as frequently as in the smaller ones nearer the cathode surface. This indicates that powerful stresses occur when, if contraction were a function of grain-size, they should be slight or non-existent. It looks, therefore, as if contraction is, in the case of any one metal, some function of, or dependent upon, the thickness of the deposit rather than of, or on, grain-size. Some of Dr. Vuilleumier's own results point to this, though they are not consistent from metal to metal. Those for nickel, contained in Tables I and II, show that the contraction tends to a minimum as the deposit thickens. On the other hand, increasing acidity slowed up the pointer, and it is known that acidity causes the structure of a deposit to be fibrous and prevents increase of grain-size.[10] Moreover, the deposits formed by Dr. Vuilleumier must have been so thin (even if the cathode efficiency was 100 percent) that no great increase of grain-size could have occurred, even though agitation was not employed.

I quite agree with Dr. Vuilleumier that the peeling of nickel deposits is p r i m a r i l y due to contraction.

Despite the foregoing criticism, which is intended to be constructive, and not destructive, of some of Dr. Vuilleumier's conclusions, I would like to express my appreciation of the value of the contractometer method in the study of the phenomena of metal deposition.

M. R. Thompson[11] (*Communicated*): At the Bureau of Standards we have not yet set up a contractometer, but have found

[8] See "On the Electrodeposition of Iron," Fig. 59 (published by the Stationery Office, London) and also Jour. Iron & Steel Inst., 1921, **103**, Fig. 3 and 10.

[9] In unpublished results.

[10] Cf. for nickel. M. R. Thompson, Trans. Am. Electrochem. Soc., 1922, **41**, 333 and for iron, W. E. Hughes, Trans. Far. Soc., 1922, **17**, 442.

[11] Bureau of Standards, Washington, D. C.

many of the ideas in the original article of Kohlschütter and Vuilleumier helpful in considering the effect of various conditions and impurities upon nickel deposition. In order to develop the relation between some of Dr. Vuilleumier's conclusions and the recent work on acidity, we prepared some of his typical solutions and measured the pH. The hydrogen-ion concentrations obtained by us were probably approximately the same as those of the solutions used by him. The results show that none of the contractometer experiments were performed with solutions having a pH in the usual range employed in commercial plating and electrotyping. This fact does not detract from the value of these experiments in pointing out certain relationships; it simply emphasizes the desirability of extending these experiments into the range of pH between, *e. g.*, 5.5 and 6.5 and co-ordinating them with commercial practice.

The following results obtained by us may be of interest in connection with the consideration of Dr. Vuilleumier's conclusions.

Reference in Dr. Vuilleumier's paper Table	$NiCl_2$ Conc. *N*	Additional Substances Used	Conc. of Additional Substances *N*	pH	Method of Measurement
I (a and b).	0.25	CH_3COOH	0.17	2.6	Hydrogen electrode
I (c).....	0.25	CH_3COOH	0.20	2.5	Hydrogen electrode
II and IV...	0.25	HCl	0.02	1.7	Hydrogen electrode
V.....	0.25	NH_4Cl NH_4OH	1.00 0.25	7.8	Cresol red Indicator
VI (32)....	1.00	H_3BO_3	0.08(M)	3.6	Brom phenol blue Indicator
VI (6b)....	1.00	NH_4Cl	1.00	3.6	Brom phenol blue Indicator

In the case of the solutions mentioned in Tables IV and V, measurements were made without adding the various foreign metal salts, but the latter would not probably alter the above pH values materially.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 22, 1922, President Schlueder-berg in the Chair.

ELECTRIC HEAT, ITS GENERATION, PROPAGATION AND APPLICATION TO INDUSTRIAL PROCESSES.[1]

By E. F. Collins[2]

Abstract.

The development of electric heat by passage of current through solid resistors, through liquid and through gaseous media is discussed at length, referring in particular to the fundamental theoretical principles. An efficient and commercial electrical heating apparatus must be constructed with due regard to chemical reactions taking place, to the effect of mechanical changes, such as expansion with heat, to physical factors such as heat transmission and heat emissivity and to the comparative cost and operating factors. [C. G. F.]

We may as well assert at the outset that heat generated electrically is not different, *per se,* from that generated by combustion or friction. We must, however, credit electric heat, broadly speaking, with advantages which accrue due to its generation free from contaminating products, as from combustion, and because of its very perfect heat control and propagation; not to mention its more perfect conservation.

The methods generally employed for the conversion of electric energy for industrial heating may be outlined as follows:

1. Heat may be developed by the passage of current through solid, laminated or granular conducting medium or "resistor."

(a) The conducting medium may consist of material that is to be treated.

(b) The heat developed in the resistor may be transferred to the charge by conduction, convection or radiation, or by all three.

[1] Manuscript received August 16, 1922.

[2] Engineer, General Electric Co., Schenectady, N. Y.

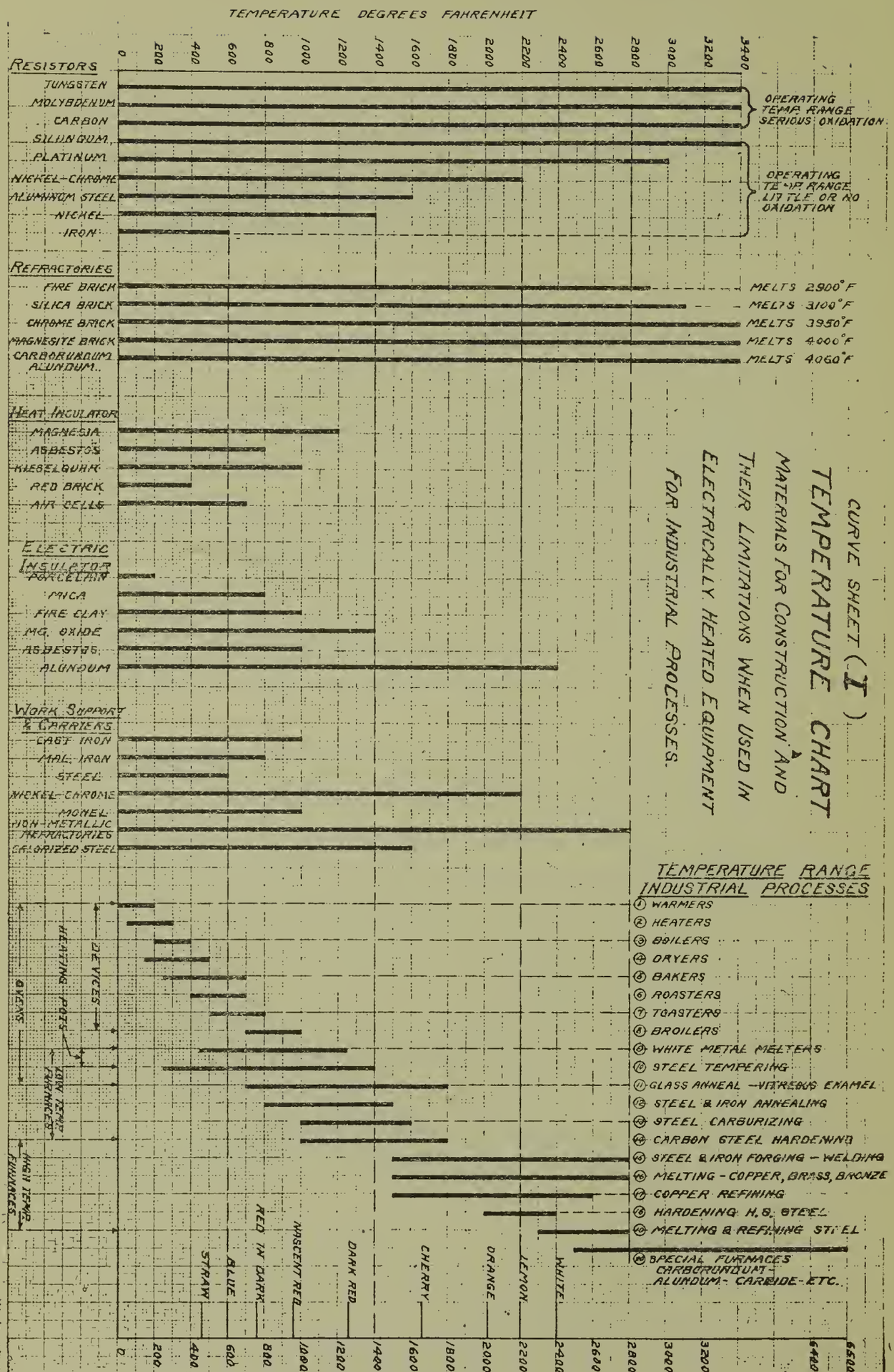

TEMPERATURE DEGREES FAHRENHEIT
0 200 400 600 800 1000 1200 1400 1600 1800 2000 2200 2400 2600 2800 3000 3200 3400
RESISTORS
TUNGSTEN
MOLYBDENUM
CARBON
SILUNDUM
PLATINUM
NICKEL-CHROME
ALUMINUM STEEL
NICKEL
IRON
OPERATING TEMP. RANGE SERIOUS OXIDATION
OPERATING TEMP RANGE LITTLE OR NO OXIDATION
REFRACTORIES
FIRE BRICK
SILICA BRICK
CHROME BRICK
MAGNESITE BRICK
CARBORUNDUM
ALUNDUM
MELTS 2900°F
MELTS 3100°F
MELTS 3950°F
MELTS 4000°F
MELTS 4060°F
HEAT INSULATOR
MAGNESIA
ASBESTOS
KIESELGUHR
RED BRICK
AIR CELLS
ELECTRIC INSULATOR PORCELAIN
MICA
FIRE CLAY
MG. OXIDE
ASBESTOS
ALUNDUM
WORK SUPPORT & CARRIERS
CAST IRON
MAL. IRON
STEEL
NICKEL-CHROME
MONEL
NON-METALLIC REFRACTORIES
CALORIZED STEEL
CURVE SHEET (I)
TEMPERATURE CHART
MATERIALS FOR CONSTRUCTION AND THEIR LIMITATIONS WHEN USED IN ELECTRICALLY HEATED EQUIPMENT FOR INDUSTRIAL PROCESSES.
TEMPERATURE RANGE INDUSTRIAL PROCESSES
1 WARMERS
2 HEATERS
3 BOILERS
4 DRYERS
5 BAKERS
6 ROASTERS
7 TOASTERS
8 BROILERS
9 WHITE METAL MELTERS
10 STEEL TEMPERING
11 GLASS ANNEAL — VITREOUS ENAMEL
12 STEEL & IRON ANNEALING
13 STEEL CARBURIZING
14 CARBON STEEL HARDENING
15 STEEL & IRON FORGING — WELDING
16 MELTING - COPPER, BRASS, BRONZE
17 COPPER REFINING
18 HARDENING H.S. STEEL
19 MELTING & REFINING STEEL
20 SPECIAL FURNACES CARBORUNDUM - ALUNDUM - CARBIDE - ETC.
HEATING DEVICES
ALL ITEMS
HEATING PADS
LOW TEMP FURNACES
HIGH TEMP FURNACES
STRAW
BLUE
RED IN DARK
NASCENT RED
DARK RED
CHERRY
ORANGE
LEMON
WHITE
TEMPERATURE DEGREES FAHRENHEIT

Fig. 1

(c) A readily controllable source of heat may be generated between a fixed and a movable carbon electrode, their distance apart being maintained so that the current flow through granular carbon lying between the faces gives rise to many chains of series and multiple contact arcs enveloping adjacent electrode faces.

II. Heat may be developed by the flow of current through a liquid or fluid conductor:

(a) Electrolytic

(b) Non-electrolytic.

III. Heat may be developed by flow of current through gas or air.

(a) Arc furnaces in which electric arcs play between two or more electrodes near material to be heated, or between one or more carbon electrodes and the material to be heated.

Industrial processes to which electric heat may be applied naturally group themselves into more or less well defined classes, when considered from the standpoint of temperatures required. Such classes are popularly known as—(1) warmers, (2) heaters, (3) boilers and compound melters, (4) dryers, (5) bakers, (6) roasters, (7) toasters, (8) broilers, (9) white metal melters, (10) steel drawing or tempering, (11) glass annealing and vitreous enameling, (12) metal annealing and normalizing, (13) steel carburizing, (14) carbon steel hardening and heat treating, (15) steel and iron forging, (16) melting non-ferrous metals, (17) copper refining, (18) hardening high speed alloys, (19) steel melting and refining, (20) special furnaces.

These processes are commonly carried out in classes of equipment commonly designated as (1) devices, (2) heating or melting pots, (3) ovens, (4) heating furnaces, (5) melting furnaces, (6) special high temperature furnaces.

An outline of the above classification is shown on Fig. 1. Here also are shown materials suited for construction to operate successfully at the different temperatures.

In order to get before us the first principles of heat application clearly, perhaps it may not be amiss to review briefly the most modern conception of what heat energy really is. Early conceptions of heat were that it was a fluid, "caloric," so-called, which entered into combination with matter and thus gave different forms

to matter. For example: Ice plus "caloric" gave water, and water plus more "caloric" gave steam. In other words, heat was supposed to be a material fluid.

When a solid was touched by the ancient physicist he usually noted two distinct sensations: one a sense of mechanical resistance to force, and a second sensation of heat or the absence of it cold. The sensations of heat and cold led him to conclude that there was some property of external matter upon which they depended, and natural philosophy suggested that this property was possessed by the living body, and that the sense of heat was an exchange of this property between the body and external matter.

Bacon early expressed the opinion that heat was due to a "brisk agitation" of the parts of a body, and Robert Boyle concurred in the opinion. Count Rumford in 1779, after tests for heat developed by abrasion of metal with a boring tool, concluded that the heat excited was due to motion. Thus he anticipated the non-materiality of heat at this time, but it was left to Sir Humphrey Davey to demonstrate later, in 1799, the real nature of heat, which he did in melting two pieces of ice by rubbing them together. This proof was only accepted, however, generally fifty years later, when Joule announced, in 1849, that his experiments gave a definite ratio of work to heat. This then called for a mechanical theory of heat.

Without following the development to the present time, let us content ourselves with reviewing briefly the theory of heat which scientists present today. It may be remarked at once that the present theory employs the laws of mechanics, and we are told that the same laws apply broadly to heat, light and electricity. In other words, these are only different manifestations of energy, and their phenomena follow identical laws. Hence equations for the flow of electricity are analogous to those for the flow of heat through thermal circuits.

Modern theory still associates heat with matter, the two being inseparable, unless it be possible to reduce matter to the absolute zero of temperature.

In order to outline briefly the interlinking of heat, light and electricity, it seems best to note first present-day conceptions of the constitution of matter.

Whereas the atom was formerly supposed to be the smallest particle of matter, it is now held that the atom is really a planetary system, consisting of a nucleus about which are grouped electrons, similar to the planets of our own solar system about the sun. The nucleus carries a charge of electricity and the electrons likewise a charge of the opposite polarity. All matter is built up from such atoms, differing only in different substances by the number of electrons which they carry.

Now electric charges in motion on electrons are electric currents. And since the electric current and magnetism are inseparable, these moving changes give rise to electrostatic and electromagnetic fields of force. As a consequence, like charges on electrons repel each other electrostatically and attract each other magnetically. The converse is true of opposite charges.

In the broadest sense space is electro-magnetic. Like electrons moving in the same direction in space attract each other, and at some speed the action of the static charge will balance this attraction. Matter, then, in all forms, systems of electrons in motion, is an electro-magnetic system. It thus follows that all properties of matter and all forms of energy are electromagnetic and electrostatic. If the above be true, then we may expect to find throughout the universe electric waves with periodicity from zero to at least that of radium emanations.

With this in mind let us look at Fig. 2, which is a heat curve, so-called, of the solar spectrum. Here we see a band of wave lengths from about 0.0004 mm. to 0.00065 mm., which embrace all colors of the visible spectrum. Wave lengths longer or shorter than these are invisible to the eye. Hence this band of electromagnetic waves we know as light. It will also be noted that this same band of waves are on the heat energy curve. This heat energy curve, however, extends on both sides of the visible spectrum, and the most intense heat rays are invisible and longer than the light waves.

From the foregoing reasoning and the evidence from Fig. 1, coupled with the fact that light waves have been demonstrated experimentally to be magnetic, we must accept the conclusion that light, heat and electricity are each governed by the same fundamental laws of electro-magnetism and electricity. Hence heat is

simply a state of matter, and the heat of a body is simply energy of motion, or kinetic energy plus potential energy of position of its constituent atoms or molecules.

From the above it follows that the quantity of heat energy

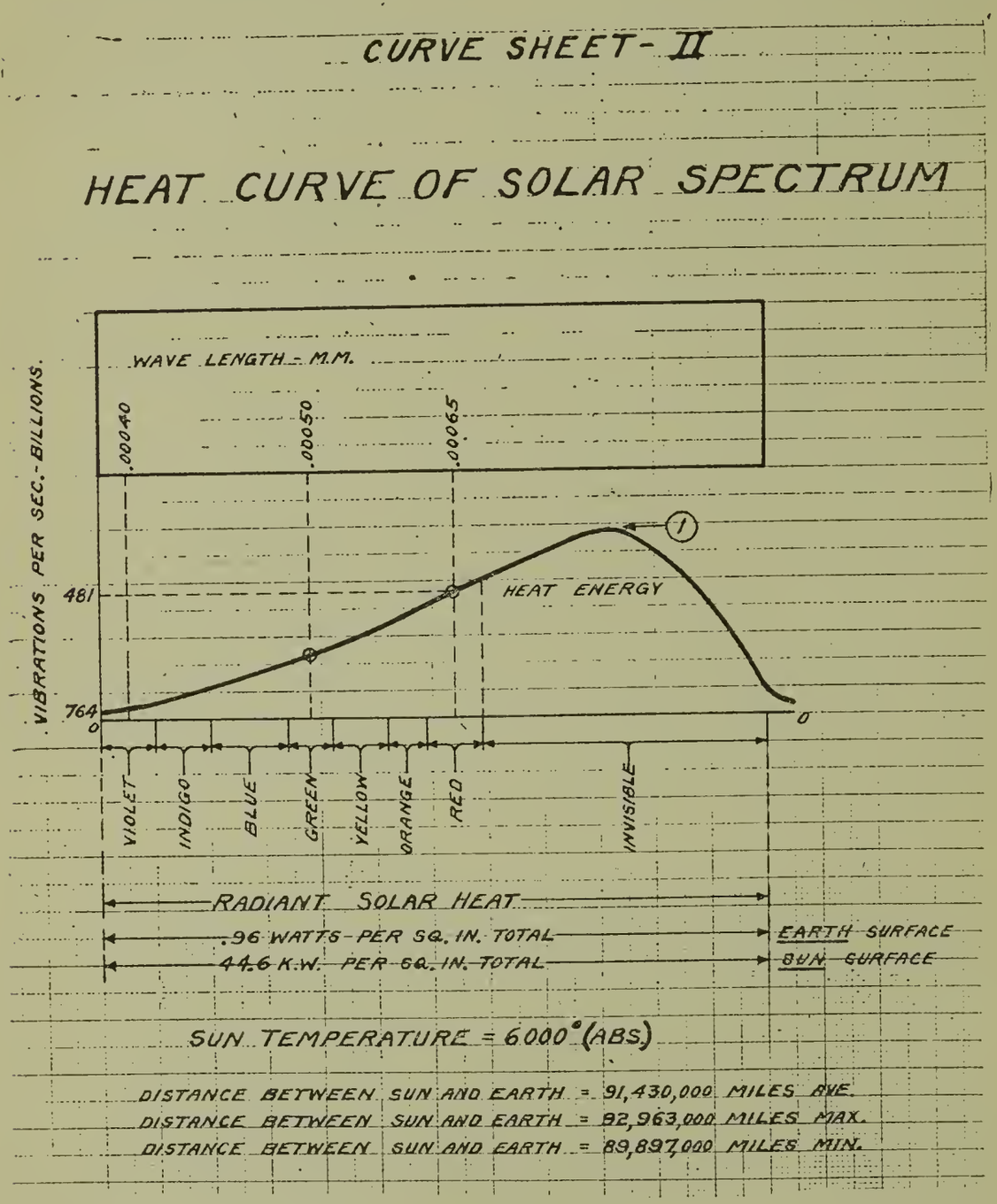


FIG. 2

which a body possesses is dependent upon its m a s s , the velocity of its atomic components, and the arrangement of these systems relatively. Hence we find, not unexpectedly, that different substances take different quantities of heat to change them one degree in temperature. This we know as the "specific heat" of that body,

the specific heat of unit volume being the quantity of heat compared to that required by water to raise a unit volume one degree in temperature. This is, then, really the specific heat capacity of unit volume, and is analogous to the capacity of the electric condenser save that it varies somewhat, usually with temperature.

Now the quantity, Q, of electricity to charge a body or condenser is $Q = CY$, where Y is the potential impressed and C the capacity.

If we denote the average thermal capacity of a body by K, then the quantity of heat possessed by the body is $Q = KT$, where T is the temperature to which the body is heated. Here we see, then, that temperature is simply a measure of heat potential and nothing more, and is a measure of the potential heat energy of the body when referred to the absolute zero of temperature T_0. It follows that the heat imparted for a change in temperature from T_1 to T_2 is $(T_2 - T_1)\ K = Q_1$. This relation is true where matter does not change its form between T_1 and T_2, *i. e.*, does not change from solid to liquid or from liquid to gas. In such case the total heat

$$Q = (T_2 - T_1)\ K + H_L,$$

where H_L is latent heat or potential energy of relative position of the component parts of matter.

The above formulæ refer to static or stored heat. In practice advantage is taken of this property of matter to secure proper "heat ballast" in heating devices. This heat ballast may be for the sake of more uniform temperature control where fluctuating demands occur, or for the sake of giving a comparatively low constant heat input, and yet satisfactorily meet sudden high intermittent demands for heat energy without regard for close temperature control. Heating equipment requiring "heat ballast" or "storage" should have the parts which so function constructed of materials with high specific heat values per unit volume, at the temperatures required for normal operation.

Fig. 3 shows the heat storage for mild steel at temperatures from 32° F. to about 2,600° F. (0° to 1,427° C.) in B. t. u. per lb.

Table I gives some values of relative heat storage compared to water as base. Where heat capacity is undesirable, as in apparatus requiring quick heating up or quick temperature changes, or

in cases where ovens open frequently to receive and discharge their contents, the engineer chooses materials from the lower part of the table or their equivalents. Likewise supports and carriers for work being treated should use material with the lowest thermal capacity and total weight consistent with dependability. Heat retaining walls should be built of materials the total thermal capacity of which, together with that of carriers and supports, will not exceed the amount necessary for "thermal ballast."

TABLE I.

Relative Heat Storage of Materials.

Water	1.00
Carborundum	0.58
Magnesite	0.60
Nickel	0.70
Soft steel	0.50
Cast iron	0.50
Glass	0.50
Fire clay	0.45
Brass and bronze	0.43
Quartz	0.42
Oak wood	0.36
Silicon	0.33
Pine	0.22
Infusorial earth	0.007
Air	0.00003

On the other hand, "thermal ballast" in furnaces should not be sacrificed generally for the sake of quick heating up from cold.

Thus far we have considered heat in the static state. Since heating equipment is essentially arranged to transfer heat from its source or point of generation to the material under treatment, the propagation of heat is a vital part of the economics of heating.

Heat may be transferred from one point to another by three general methods, viz., conduction, convection, and radiation.

When heat is transferred from one body to another by c o n d u c t i o n, the two bodies must be contiguous or in contact, and one body must have a higher heat potential or temperature than the other. The heat exchange between the two bodies will be a steady, fluctuating or alternating flow, depending upon the value and sign of the heat potential difference with time. Hence we may say there are constant currents of heat, and pulsating or

fluctuating currents, as well as alternating currents flowing in the thermal circuit entirely analogous to the flow of current in the electric circuit. We may also have thermal circuits in which

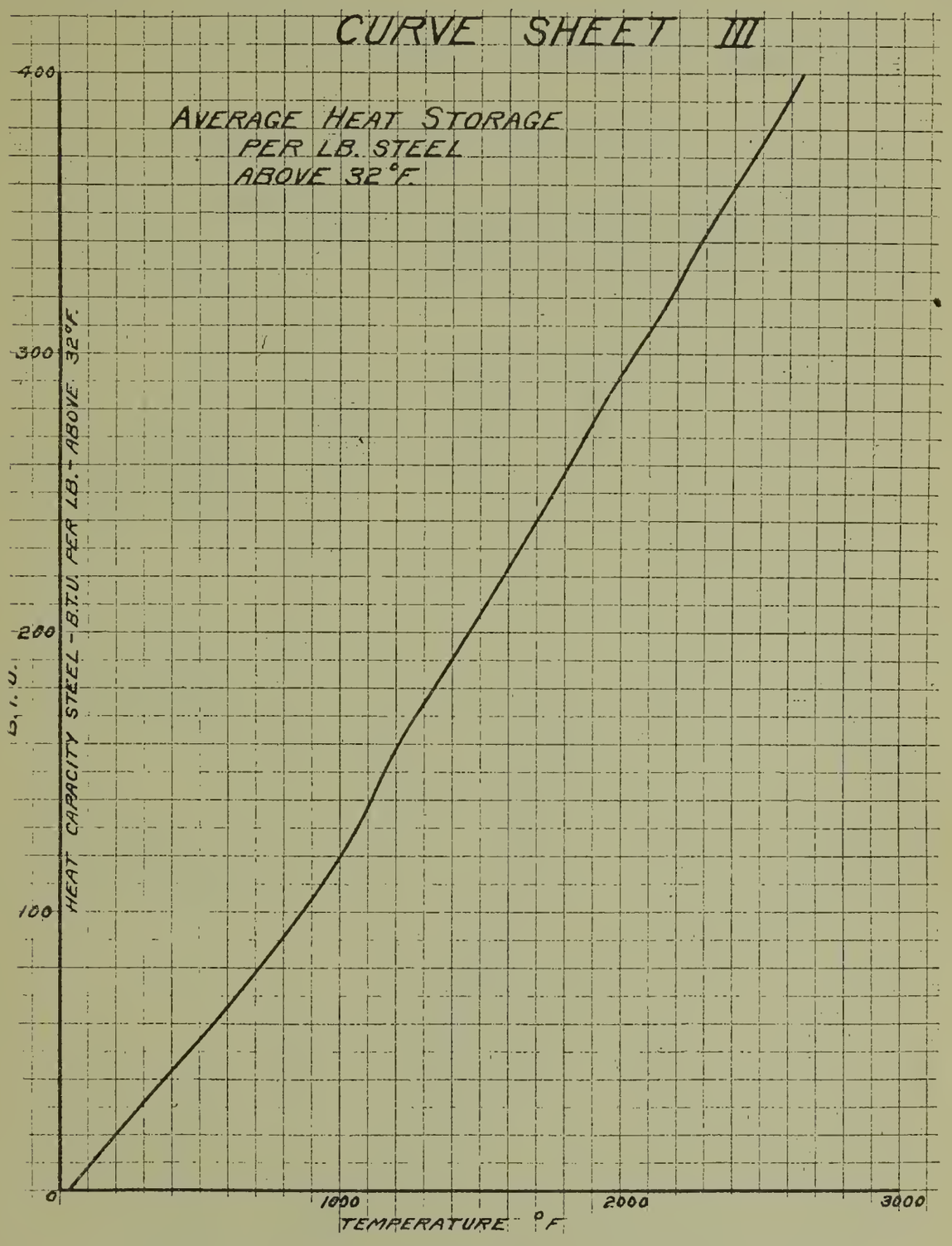


FIG. 3.

fluctuating, alternating, pulsating or transient heat flow is superimposed upon constant heat flow. In fact, the ordinary fuel-fired furnace gives a bewildering mixture of such currents.

In the electric furnace it is possible to choose in most cases with what type of flow heat will be transferred, and hence the control and calculation and prediction of results is more readily and surely accomplished. Likewise such control of conditions of heat transfer by conduction makes sure duplication of heat cycles according to prescribed demands.

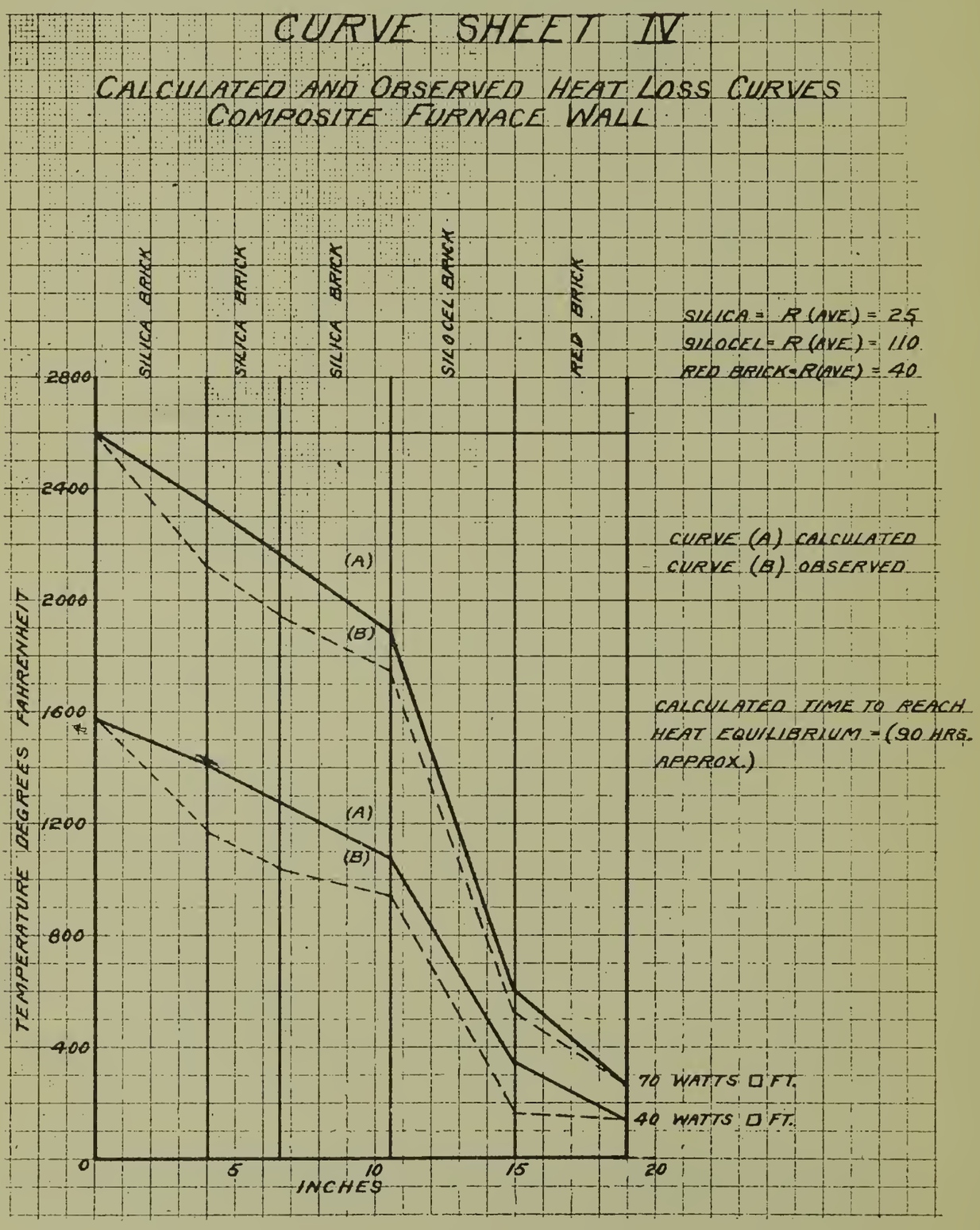


FIG. 4.

To illustrate the above, suppose we want a perfectly uniform flow of heat to the charge. We will then feed power at a uni-

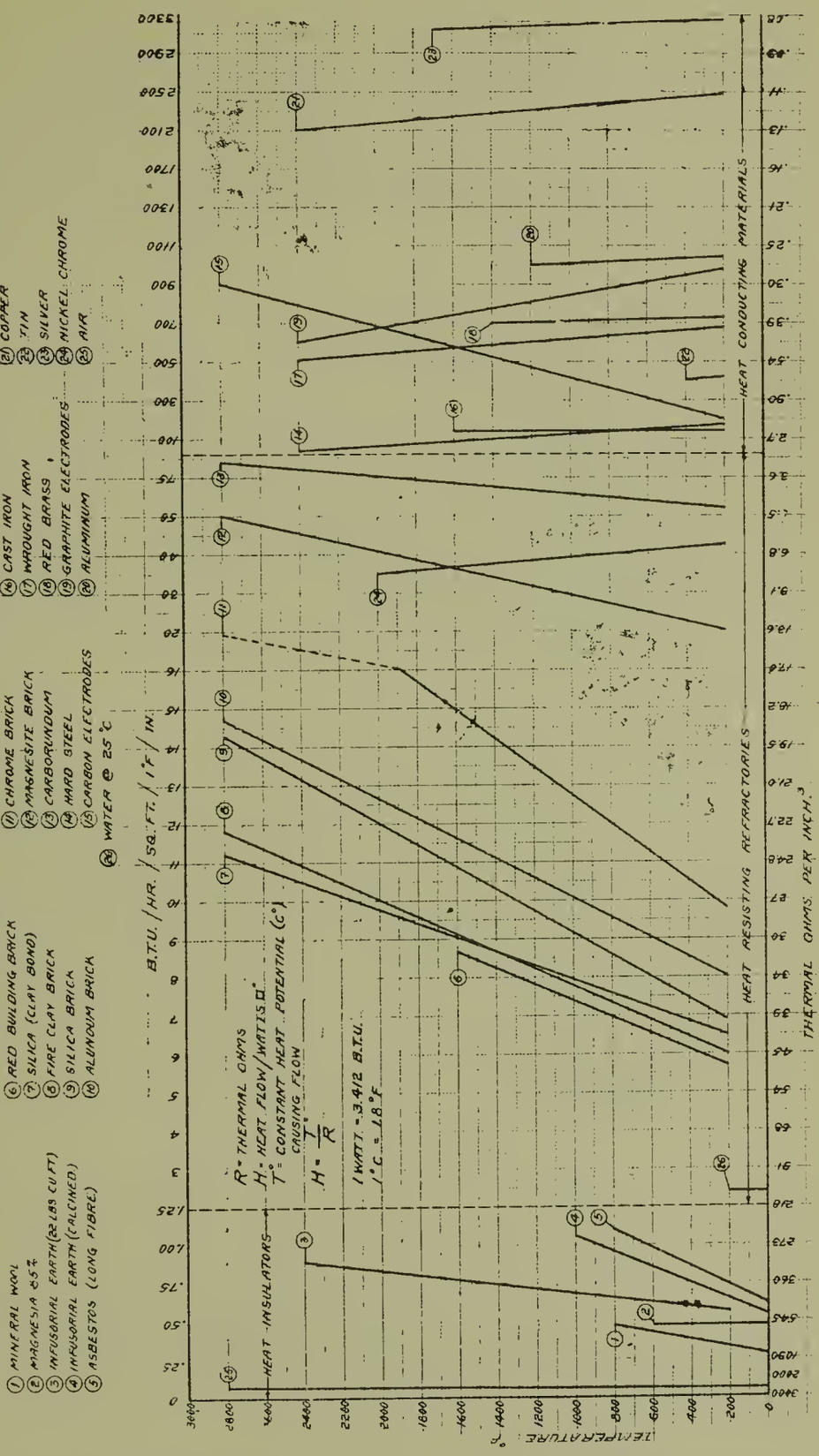


FIG. 5.

form rate to our electric resistor at a constant voltage; if a slightly less stringent requirement for steady heat flow exists, we may for the sake of automatic control use an interrupted or

variable voltage actuated by a temperature or heat control instrument and compensate for voltage changes more or less com-

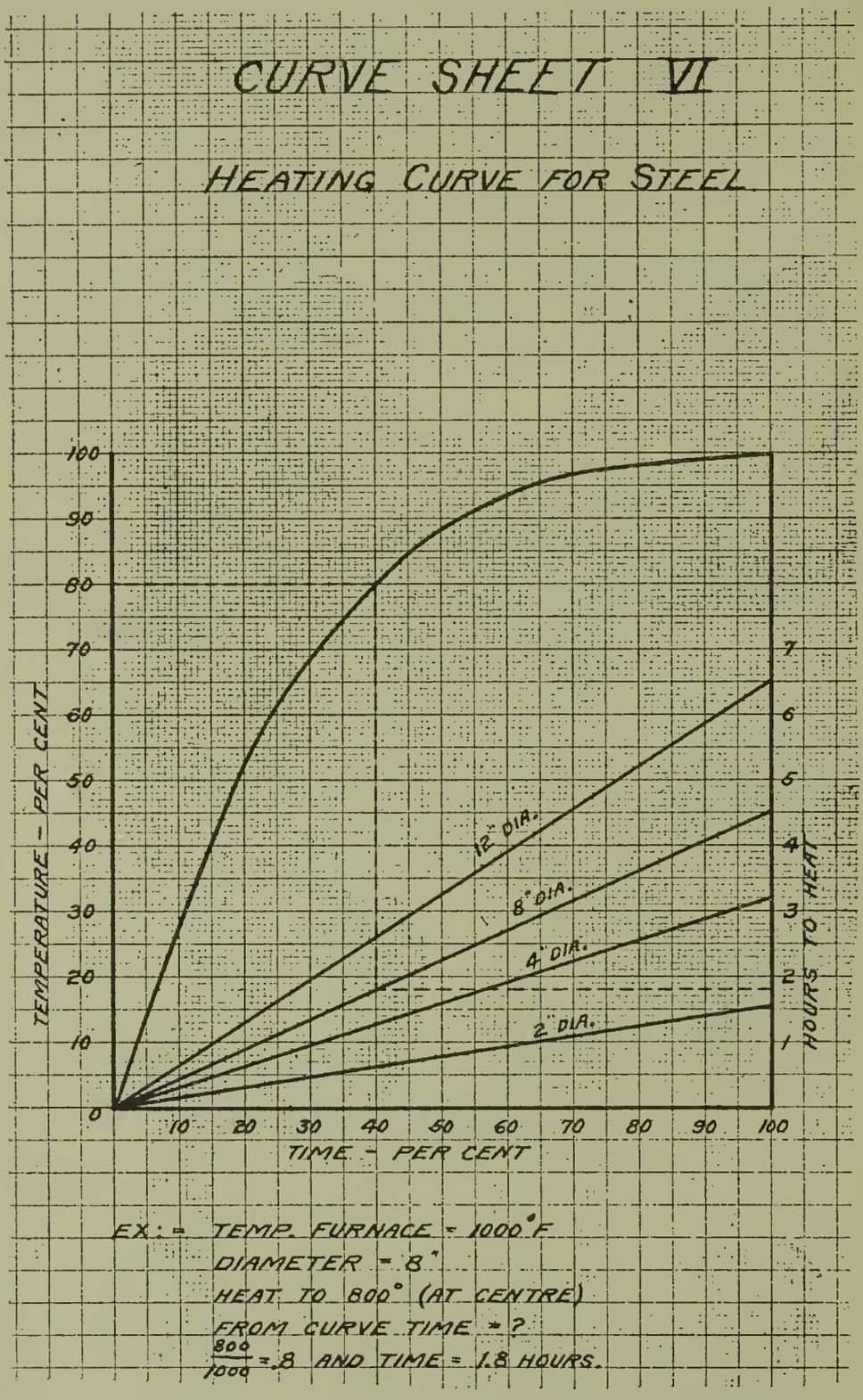


FIG. 6.

pletely through the use of heat ballast, which would superimpose an alternating heat flow upon the fluctuating flow from the source, and in such phase relation as to give sufficiently steady total heat

flow. The action of the heat ballast is automatic, and when properly arranged aids greatly in securing uniformity of heat control.

Fourier's fundamental equations for "the linear motion of travel of heat" involves thermal resistance and thermal capacity as controlling factors, and they may be used with proper modifications to calculate many desirable heat quantities entering vitally any new furnace design.

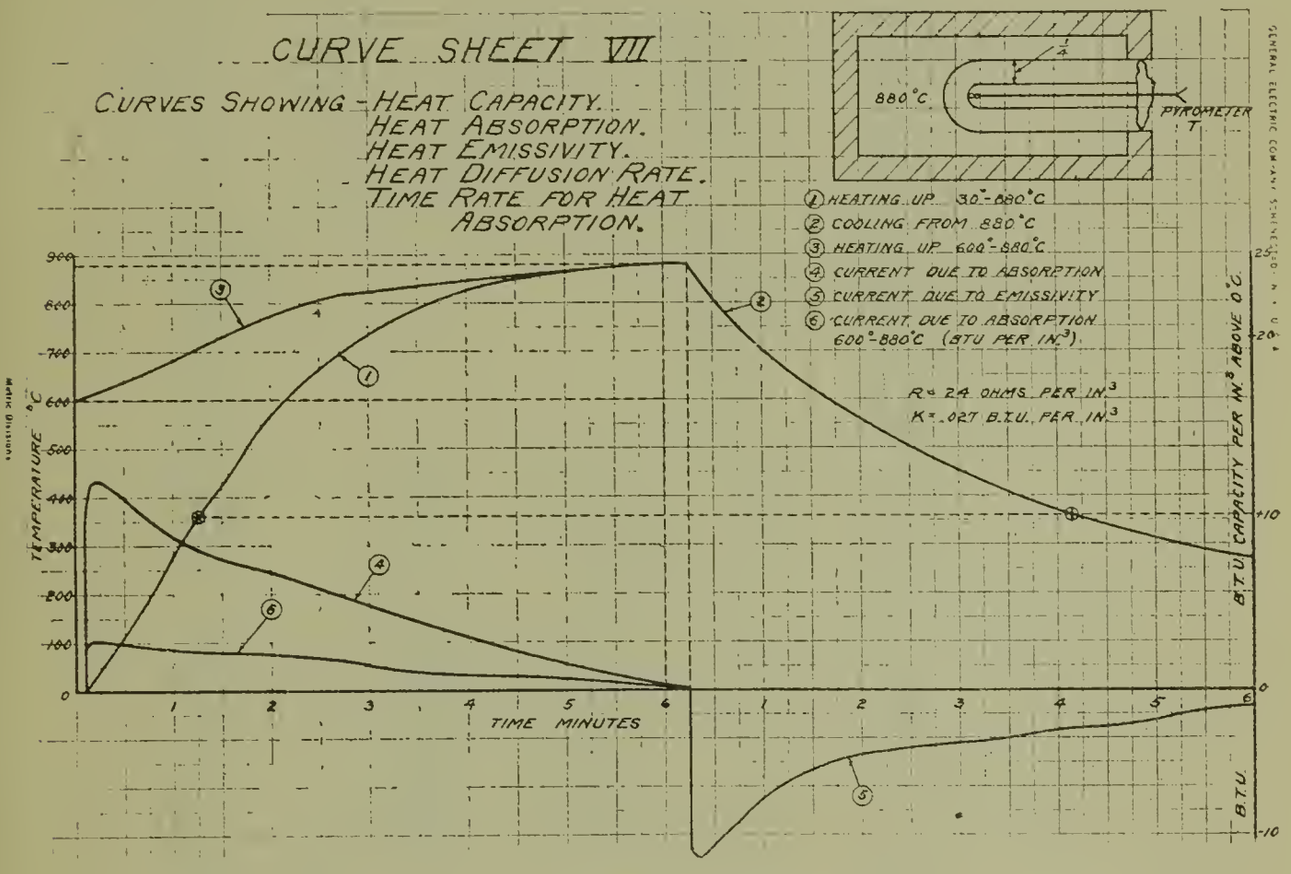


FIG. 7.

Thus, if R be the resistivity and K be the thermal capacity of unit volume, then the quantity K/R is known as the thermal diffusivity. Hence such results of diffusion as given in Table II may be obtained if the diffusion of one material is known or calculated from known values of R and K corresponding to various materials. Fig. 5 gives resistance values for materials much used in heating work. Calculations give 90 hours approximately as time for wall in Fig. 4 to reach temperature equilibrium.

As an example, such data may be used to determine as closely as required the length of time required for furnace walls to

Table II.

Values of heat capacity, thermal resistance and rate of heat diffusion.

Material	K = Heat Cap 1° C. B.t.u. per cu. in., Av.	Thermal ohms per cu. in.			Rate of heat travel or diffusion
		Av.	High	Low	
	K	*R*			Min. per in.
Cast iron	0.028	2.5	....	....	2.3
Wrought iron	0.32	1.49	....	....	1.22
Steel	0.33	2.22	....	....	1.82
Copper	0.030	0.26	....	....	.22
Brass	0.027	0.77	....	....	0.73
Aluminum	0.019	0.27	....	....	0.36
Silver	0.020	0.08	....	....	0.10
Tin	0.013	0.57	....	....	1.14
Pine wood	0.008	640.00	....	....	2080.
Oak wood	0.013	550.00	....	....	1100.
Birch wood	0.011	500.00	....	....	1170.
Bichrome	0.032	6.20	....	....	5.2
Glass	0.018	90.00	....	....	130.
Graphite	0.040	0.28	....	....	0.18
			100°C.	20°C.	
Air (60° F.)	0.000011	3600.	3300	4000	8,500,000
Water	0.036	130.	....	....	93.
			2800°F.	200°F.	
Carborundum	0.021	4.00	3.15	5.0	5.2
			2800°F.	200°F.	
Silica	0.011	33.	24.0	42.0	78.
			1800°F.	200°F.	
Chrome	0.017	22.	17.0	27.0	33.
			2600°F.	200°F.	
Fire clay	0.016	32.	23.0	42.0	52.
			2600°F.	200°F.	
Magnesite	0.022	6.8	5.5	13.6	8.
Alundum	0.027	25.	....	....	24.
			2600°F.	200°F.	
Red brick	0.011	....	19.0	34.0	44.
Quartz sand—					
coarse	0.017	24.	....	....	36.
Brick dust	0.010	100.	....	....	260.
			700°F.	100°F.	
Kieselguhr	0.0025	....	427.	562	5800.

reach equilibrium. It reveals the rate of heat propagation or travel rate of heat through walls or muffles. Formulæ give the time lag for heat travel through muffles or baffles. Their use allows of calculations of the heat energy absorbed or given out during any time when the furnace is being heated or cooled.

Such calculations may be made for single or composite walls. when the thermal resistance and specific heat of wall materials are known. In Fig. 4 are plotted results of calculations for a

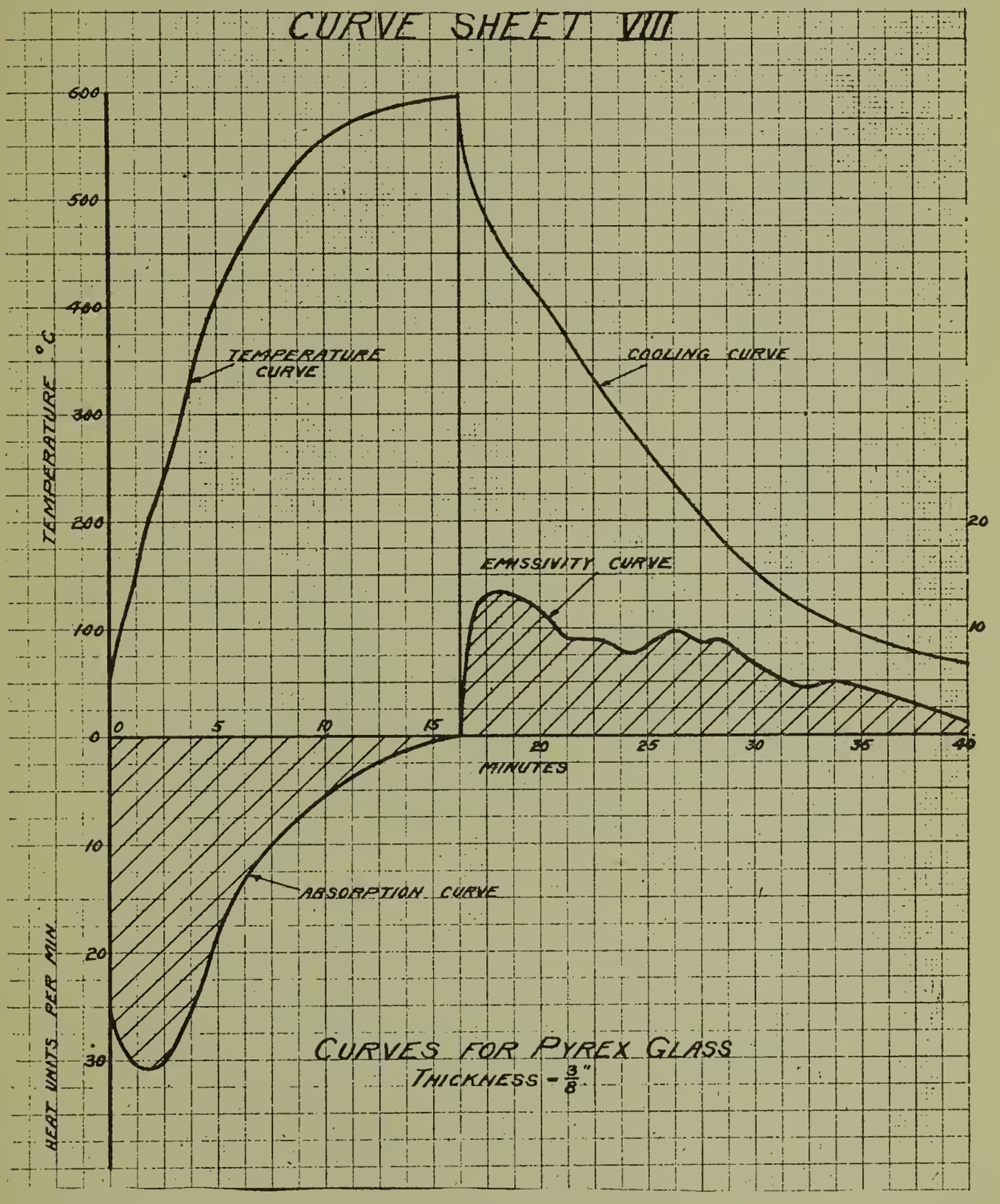


FIG. 8.

composite brick wall, the inside temperature of which is about 2600° F. (1427° C.)

It is appreciated that both thermal resistance and specific heat

vary with temperature somewhat, but average values when used give results that are as accurate as demanded by good design.

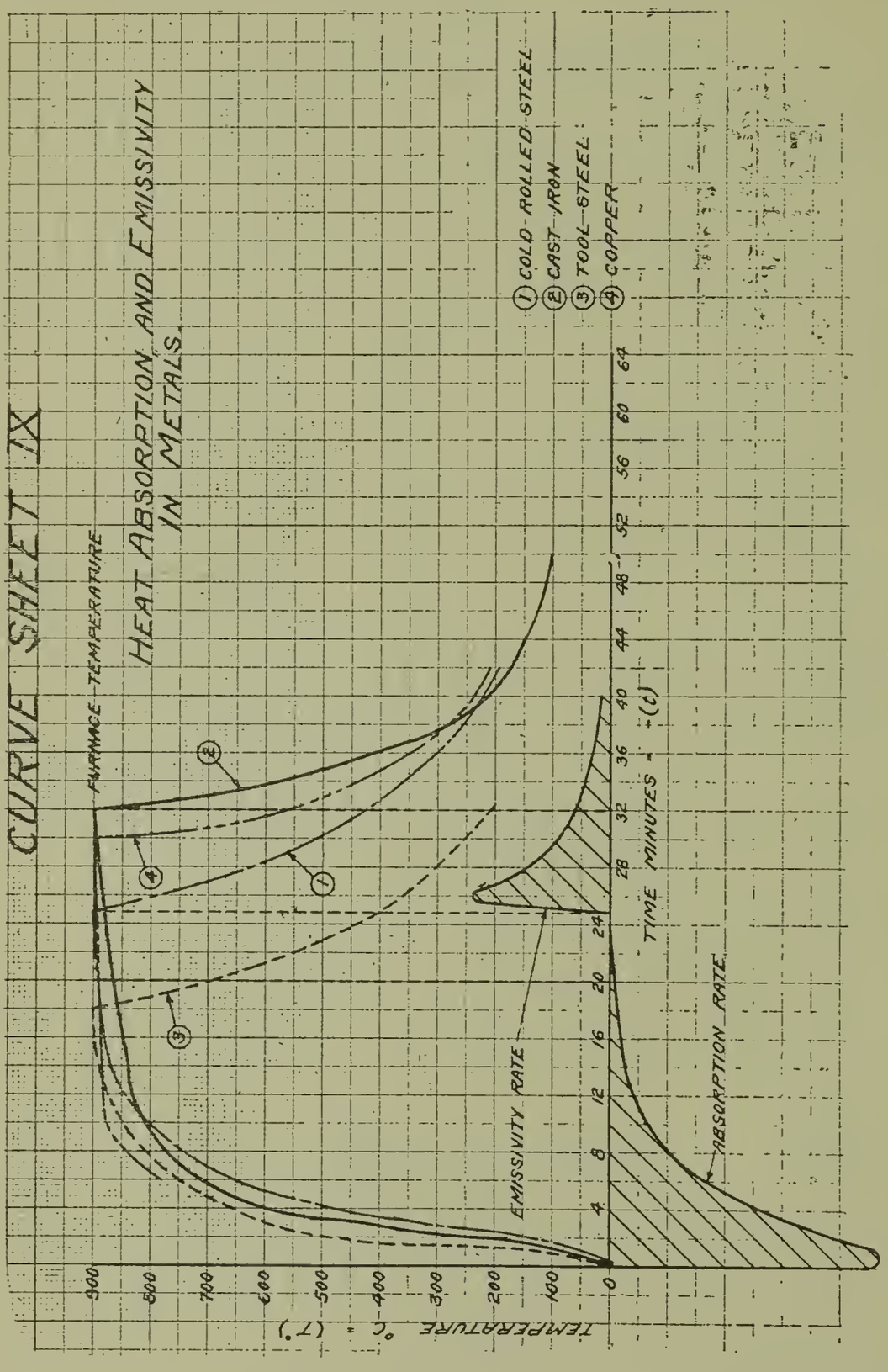


FIG. 9.

The law algebraically expressed for continuous heat flow in conducting circuits is the same as Ohm's law for direct electric currents, viz., $H = T/R$, where the current of heat flow H

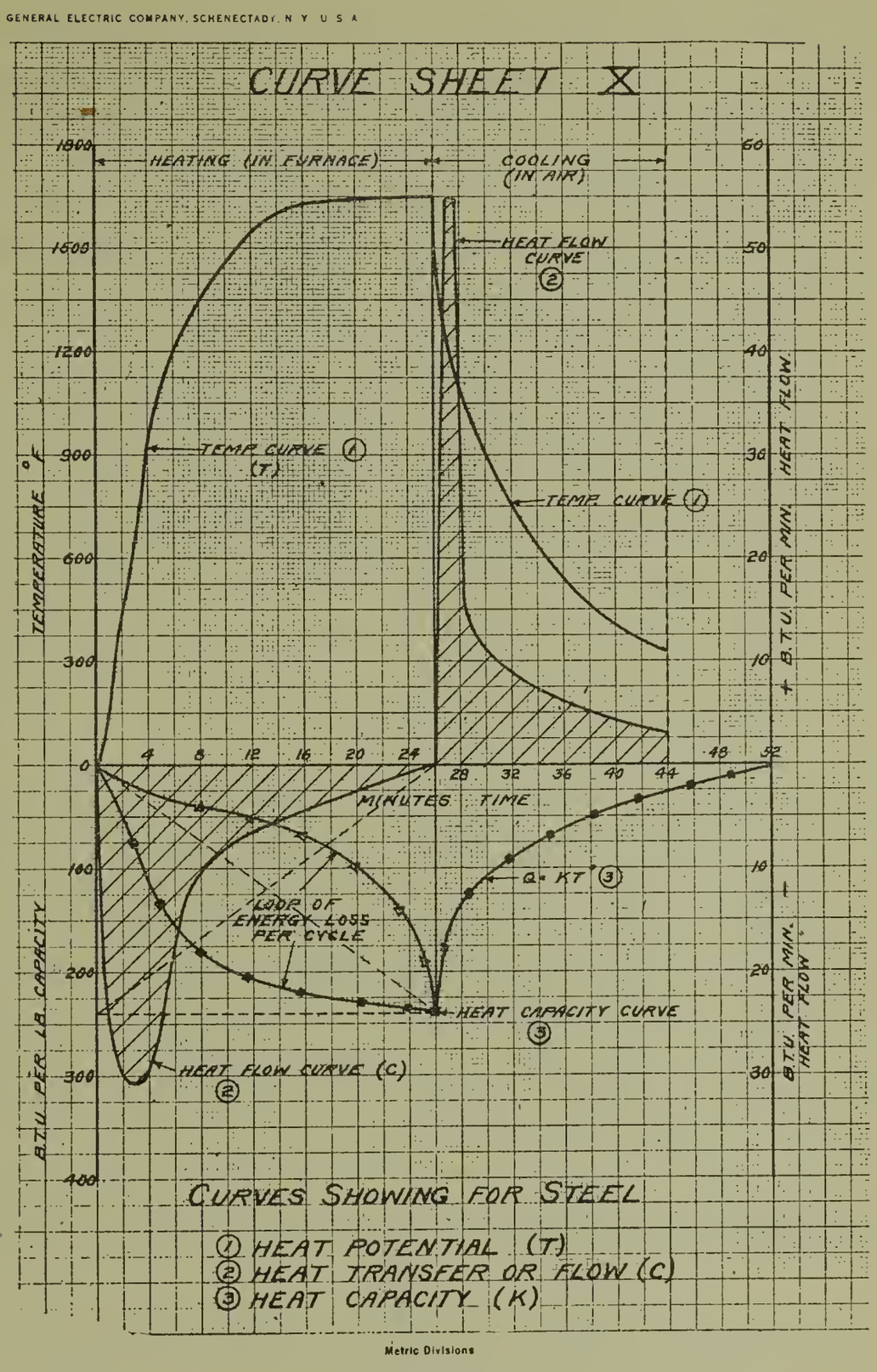

GENERAL ELECTRIC COMPANY, SCHENECTADY, N Y U S A
CURVE SHEET X
HEATING (IN FURNACE)
COOLING (IN AIR)
HEAT FLOW CURVE ②
TEMP. CURVE ① (T)
TEMP. CURVE ①
TEMPERATURE °F
+ B.T.U. PER MIN. HEAT FLOW
MINUTES TIME
Q = KT ③
LOOP OF ENERGY LOSS PER CYCLE
HEAT CAPACITY CURVE ③
HEAT FLOW CURVE (C) ②
B.T.U. PER LB. CAPACITY
- B.T.U. PER MIN. HEAT FLOW
CURVES SHOWING FOR STEEL
① HEAT POTENTIAL (T)
② HEAT TRANSFER OR FLOW (C)
③ HEAT CAPACITY (K)
Metric Divisions

FIG. 10.

equals the temperature T, divided by R, the thermal resistance of the circuit expressed in thermal ohms. This law expresses the values of current after it has become constant under a thermal potential difference of T degrees in temperature.

It is of considerable importance to know, however, the way in

which a heat current rises to its full flow under a given temperature difference and its value at any time. We readily recognize that opposing the rise of current in the thermal circuit we have the capacity of the body to absorb heat and its resistance to the flow of heat, or, in other words, its "specific heat" and "thermic resistance." This is analogous to the electric circuit with resistance and capacity. In other words, any change in temperature impressed upon a body of uniform material must be maintained for a given length of time, depending upon the quantity R/K corresponding to the material in order to secure heat equilibrium throughout the body. Recognition of this principle and modifications of it give a basis for construction of such a general curve as shown on Fig. 6, which may be used as an approximate chart for time of heating to any temperature bars of steel of various diameters, and having any initial temperatures when introduced into the furnace. The chart has been checked in many points by actual tests, and shows results sufficiently close for use in blocking out new designs of furnaces.

The fact that heat flow rate is a property of the particular material in question, is well shown in Fig. 7. Here it is seen that the time to diffuse heat through the 0.25-inch tube is the same when the impressed temperature is 280° C. and 880° C., or about 6 min. Hence the basis for the steel heating chart in Fig. 6. Also note the heat current or flow when heating up and when cooling. It is by virtue of this heat flow that the ballast effect is utilized in many furnace controls. Heat absorption and heat emissivity are well shown here. Fig. 8 shows absorption and emissivity curves for Pyrex glass, while Fig. 9 shows comparative absorption and emissivity curves for some of the common metals.

Fig. 10 shows for steel, (1) the heat potential time curve for heating and cooling, (2) the heat current flow or transient currents during the cycle, and (3) the energy loss sustained in the cycle of heating and cooling. This loss curve must be met each time a body is heated and cooled. It may be noted that here again we have the counterpart of the hysteresis loss in magnetic circuits. This curve may be readily calculated for ovens or furnaces, and account should be taken of it in the heat balance

calculations. It comes in with a value depending upon the character of construction of oven or furnace walls, and with a frequency equal to that with which operating temperatures are raised and lowered, as by opening and closing oven doors.

Having briefly considered static heat, and dynamic heat, together with its absorption, conduction, diffusion and emissivity, we will now see how heat is transferred by convection; that is, it is mechanically carried from one body to another by movements in the body of the carrier gas or fluid. These movements may be the result of mechanical agitation of the fluid, such as by a fan or blower, or it may be due to gravity acting as a result of varying densities due to the heat change itself. When a charge is heated by contact with hot gases, we have Q varies as $T^{-0.24}$, where T is the convecting plane temperature, and for gas velocity of 600 ft. per min. to 3600 ft. per min., Q also varies as $(V - 25)/25$, where V is expressed in centimeters per sec.

When two bodies are at different temperatures and are separated by a transparent medium, such as air, water, glass or ice, heat passes from one to the other, irrespective of the temperature of the intervening medium, except that its transparency may vary with temperature.

This process of heat transfer through an intervening medium is known as radiation of heat. The condition of the intervening matter, in virtue of which heat is thus transferred, is called light, and radiant heat is light if the eye were sensitive to it. Hence radiant heat is brought under the theory of light, and conversely light is annexed to heat as a magnificent outlying province of the kinetic theory of heat.

The transfer of radiant heat is according to Stephen Boltzman's law—

$$W = 5.7 \frac{T^4}{1000^4} - \frac{T_0^4}{1000^4},$$

where W = the energy in watts radiated per sq. cm., and T is the temperature of the hot body, and T_0 is the temperature of the surrounding space. Hagen and Rubens calculate the relative emissivity by the formula—

$$1 - \gamma = \epsilon = 0.365 \sqrt{\frac{\theta}{\lambda}},$$

where γ is the reflectivity of heat energy, θ is the specific electric resistivity in ohms-centimeter-units at the temperature of the body or metal, and λ the wave length of the energy in centimeters.

Substituting the average wave length for light, which according to Wien's law is $0.29/T$ cm., we get $\epsilon = 0.68\sqrt{\theta T}$, which enables us to calculate the emissivity of polished metals up to temperatures giving corrosion or oxidation.

Table III gives some values for emissivity.

TABLE III.

Emissivity of Metals.

Copper oxidized by red heat	0.74
Copper calorized	0.27
Silver pure	0.03
Cast iron (fresh machined)	0.25
Cast iron oxidized by red heat	0.65
Aluminum paint (on cast iron)	0.47
Gold enamel (on cast iron)	0.39
Monel metal (polished)	0.40
Monel metal (oxidized)	0.45

For non-metallic substances the emissivity ranges from about 0.3 to 0.9. In taking advantage of this law the furnace designer uses high emissivity materials for resistors and low emissivity for furnace enclosing walls.

When applied to resistor design we observe from $\epsilon = 0.68\sqrt{T}$ that we may increase emissivity by increase of temperature of resistor, which we may assume to be a round wire with unit radius. Hence, radiating area = 3.14 per unit length and volume, 0.78.

Now assume the wire rolled flat to a width of 1.56. Its surface becomes 2 x 1.56 = 4.12, and its emissivity is increased in the ratio of 4.12/3.14, or about 30 percent with the same material weight. Or we may write,

$$\frac{0.68}{4.12}\sqrt{T} = \frac{0.68}{3.14}\sqrt{T_1}, \text{ or } T_1 = 0.56 - T.$$

This means that for the same total emissivity we may hold the same temperature and use a ribbon 1.56 wide, or we may retain the round wire, and raise its temperature about 50 percent. This demonstrates what effect the form of material has upon the total emissivity, and illustrates the importance of this law to the de-

signer of metallic resistor furnaces where the temperature of the metallic resistor is limited.

Again, since $\epsilon = 1 - \gamma$, where γ is the reflectivity, the engineer

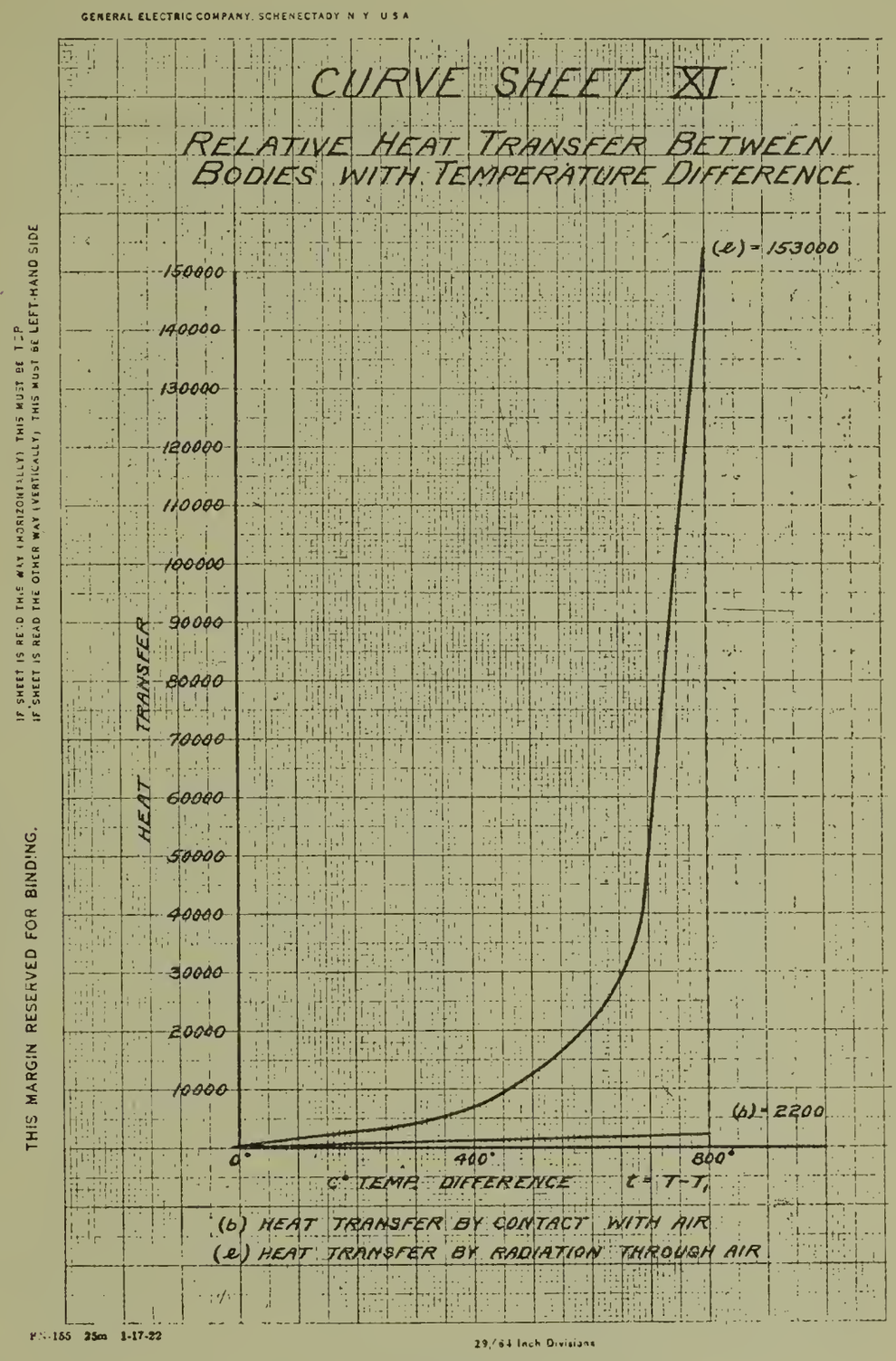


FIG. 11

will choose materials for his furnace walls from materials with comparatively low emissivity, in order to secure high reflectivity. and thus secure distribution and equalization of heat, not to men-

tion the effect upon thermal efficiency. Reflectivity is aided, of course, by re-radiation from furnace walls after they become heated.

Radiant heat is distributed according to the laws of light. It may be reflected, polarized, absorbed. Hence in a closed chamber, if the heat source is so located that the chamber and charge are uniformly illuminated when the resistors are replaced by a light source, we will get uniform distribution of heat. This is not true in free space. Here the intensity of radiation is as the square of the distance from the source of heat.

The foregoing facts are important when applied to electric furnace design involving temperatures of from 1,200° F. to 2,000° F. (649° to 1,093° C.) where the percentage of radiated to total heat ranges from perhaps 90 at the low temperature to 98 at the high.

TABLE IV.

Heat Transfer Through Air from Resistor to Black Body.

Total Heat Percent	Convection Percent	Radiation Percent	Conduction Percent	Air Velocity	Air Temp. F.
100	59.9	40	0.08	Natural	100
100	82.2	17.0	0.08	400 ft. per m.	100
100	86.2	13	0.08	200 ft. per m.	100
100	32.6	67	0.4	Natural	500
100	54.6	45	0.4	400 ft. per m.	500
100	62.6	37	0.4	2000 ft. per m.	500
100	14.2	85	0.8	Natural	1000
100	27.2	72	0.8	400 ft. per m.	1000
100	34.2	65	0.8	2000 ft. per m.	1000
100	2.6	96	1.4	Natural	1500
100	7.6	91	1.4	400 ft. per m.	1500
100	12.6	86	1.4	2000 ft. per m.	1500

Table IV gives comparative values for conducted, convected and radiated heat for 100° F., 500° F., 1,000° F., and 1.500° F. (38°, 260°, 538°, and 816° C.)

Fig. 12 shows effect of convection, both natural and forced. These results together with those of Table IV must be heeded by the engineer in designing all kinds of heating ovens and furnaces, but it is of special importance in connection with design of ovens operating at 500° F. (260° C.) or less where forced circulation,

re-circulation or compensated type of ovens are to be made use of. Such ovens are core ovens, drying ovens, etc. It will also be

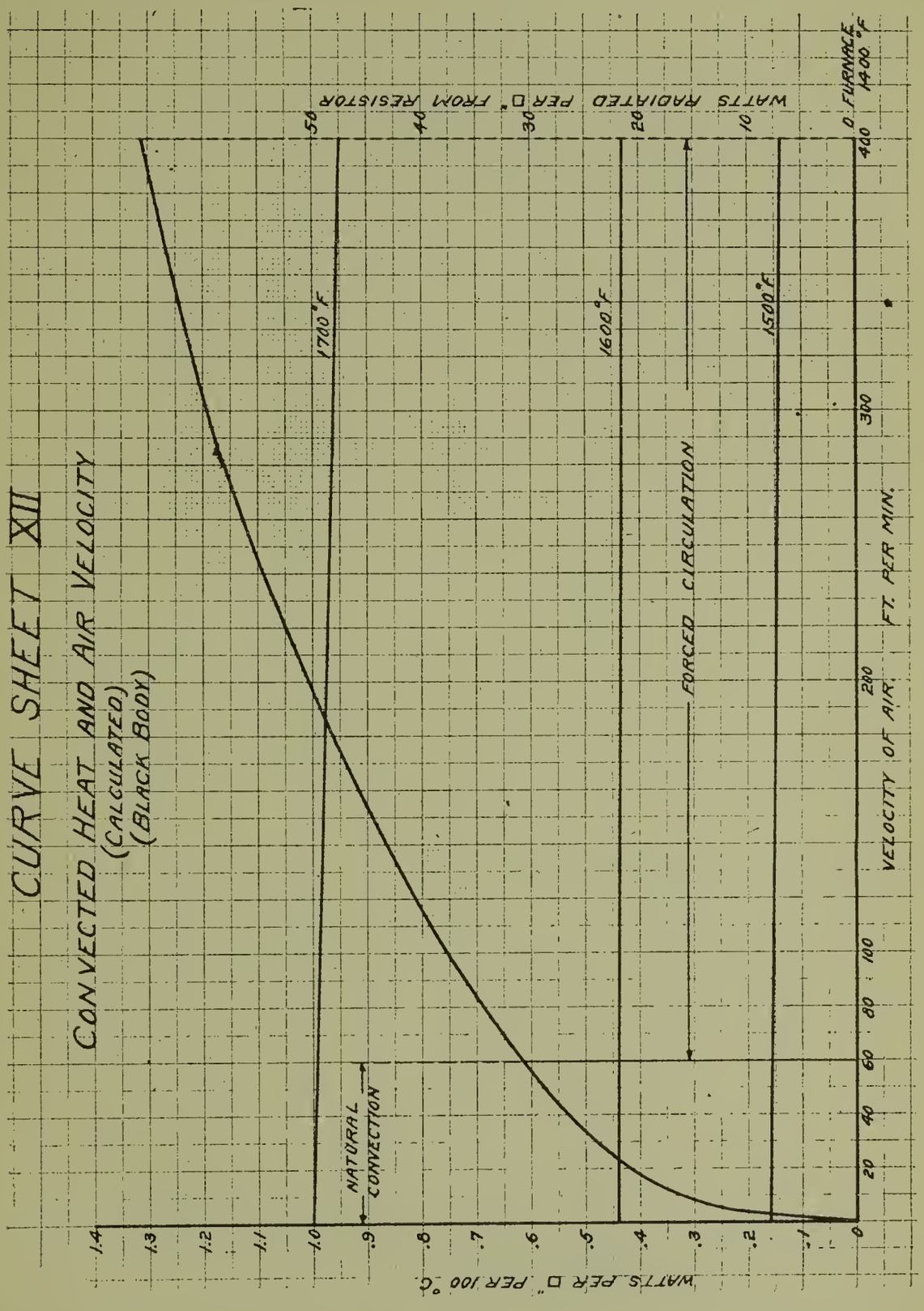


Fig. 12.

noted that circulation of furnace atmosphere can have but little influence on uniformity of temperature at the higher temperatures.

When luminous radiations are incident on a body, we are

familiar with what occurs. It has been demonstrated that non-luminous or invisible radiations produce like effects. We have bodies transparent more or less to radiant heat, and again bodies

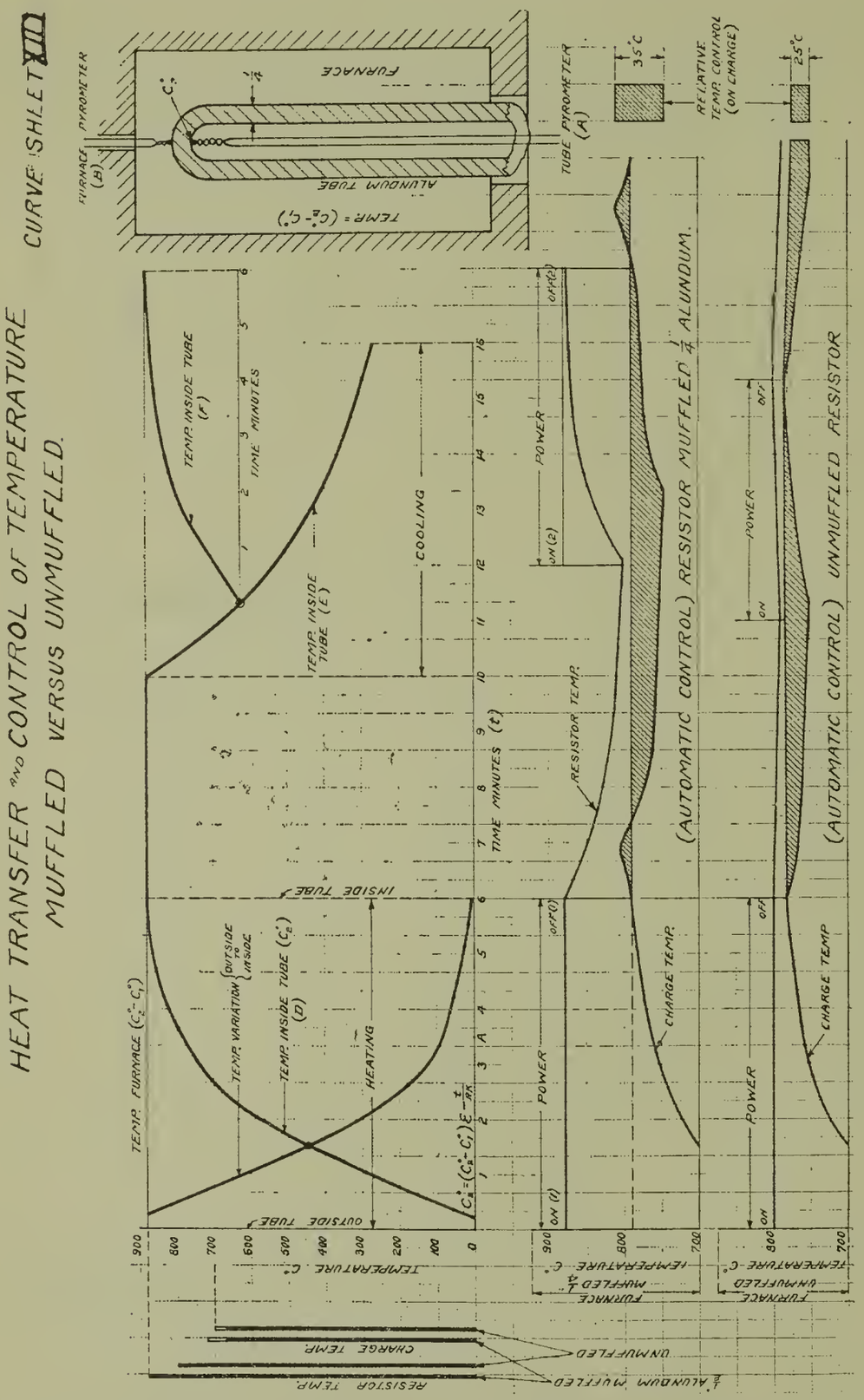


Fig. 13.

that absorb it almost wholly. In general, a part of radiant heat is reflected, a second part is transmitted, and the remaining third is absorbed by a body subjected to the radiant energy. Bodies

which transmit radiant heat, like rock salt, are called diathemous, while those like lampblack, which absorb it, are athemous. Hence matter may be assumed to have vibration rates of its own, and hence it absorbs vibrations corresponding to its own, and passes those which have a different frequency, or rejects them.

These facts make it important to the heating engineer to use great care in selecting and using materials for containers or muffles in radiant temperatures, lest he incur great handicaps in getting radiant heat to the charge to be heated. The walls of containers or muffles may be very thin and yet work a great retardation of heat supply. For example, a sheet of glass 2.6 mm. thick stops all radiant heat from blackened copper at 100° C., and all but 6 percent from copper at 390° C.

Fig. 13 shows how the 6-minute retardation of radiant heat by 0.25 inch muffle of alundum affects the control and regulation of an automatically regulated furnace where constant temperature is secured by the "off" and "on" method of control of power. It likewise shows that a higher temperature gradient must exist for the same heat transfer from resistor to work where such muffle effect exists. The sensitiveness of control is affected 40 percent and the resistor temperature is increased about 80° C. The control is more sluggish in that its period is increased about 25 percent.

Since it is difficult to find athemous materials suited to high or radiant temperatures, we have made it a rule to employ containers and muffles only when there is no possibility of avoiding their use. For they impose in general a great handicap, however carefully selected may be the material and method of their design and construction.

To sum up the deleterious effect of muffling, especially in high temperature furnaces, we have:

(a) Retardation of heat flow by muffle gives a more sluggish transfer of heat than that which would occur without muffle.

(b) For the same rate of heat transfer the resistor temperature must be higher than for the unmuffled resistor or heat source.

(c) The control of temperature of the heating charge through control of resistor temperature is less exact, due to an "under

shooting" and "over shooting" resulting from heat lag in the muffle.

(d) The same sensitiveness of automatic control of temperature cannot occur with the muffled resistor, because this would require a regulator which could anticipate the relation about to be established between temperatures on either side of muffle.

(e) Lower thermal efficiency with the same degree of heat insulation in furnace walls would be experienced, due to the higher resistor temperature required in the muffled furnace.

(f) Since life of resistor varies inversely as some power of the temperature at which it operates, it follows that for the same duty the unmuffled furnace will have the longer life.

(g) Since the metallic resistor has a temperature limit beyond which it is not practical to go, the muffle limits the safe operating temperature of the heating chamber to a lower value.

In building the outside walls of the furnace to conserve heat, we are glad to make use of materials that are diathemous.

The brief allusion to some of the more important laws of furnace design has already given a paper of greater length than intended. It is hoped that what has been said will illustrate that the proper design and application of electric heat to industrial processes requires engineering skill of the highest order. The successful application of electric heat to the varied processes met in the manufacturing world involves not only a knowledge of the particular characteristics, both physical and chemical, of the process involved, but the heating device in question should be of such design as to take account of at least the laws governing the following outlined conditions, tempered with good judgment, resulting from experience:

(1) Chemical Laws—
- (a) Chemical reactions at low and high temperatures
- (b) Oxidation, decarbonization at high temperature
- (c) Fluxing of refractories. Effect of furnace atmospheres

(2) Mechanical Laws—
- (a) Expansion and contraction with heat
- (b) Physical strength at low and high temperature
- (c) Crystal growth, with temperature
- (d) Abrasion of refractories when heated
- (e) Mechanical methods of construction

(3) PHYSICAL LAWS—

(a) Heat generation
(b) Heat conservation
(c) Heat transmission
(d) Heat absorption
(e) Heat distribution
(f) Heat storage
(g) Heat equalization
(h) Heat emissivity
(i) Heat potential
(j) Heat diffusion
(k) Heat quantity
(l) Temperature gradients
(m) Control of temperatures through control of heat flow

(4) LAWS OF ENVIRONMENT AND PSYCHOLOGY—

(a) Complete knowledge of the heating process involved
(b) More or less complete knowledge of shop methods and individuals who will use the device.
(c) Peculiarities associated with the product to be treated or methods of manufacture should be appreciated.
(d) What is the frame of mind of the operator? Will he support or antagonize a given design?
(e) Do executives realize the importance of correct furnace design, and how far will they modify methods to take the fullest advantage of new and progressive equipment offered?
(f) Does equipment afford better working conditions for the operator?

(5) ECONOMIC LAWS—

(a) Covering first cost of heating equipment
(b) Covering operation and operating cost of furnace
(c) Covering reduction of cost of product and retaining the same quality
(d) Covering increase in uniformity and quality of product and retaining the same cost
(e) Greater output for same floor space
(f) Reduction in labor
(g) Location of equipment in the line of production, etc.

Before closing I want to say a word about over-all cost of electric heating. I recently reviewed a table made up to show the cost of the electric heat treatment involved in terms of factory cost of the part. The entire cost of heat treating electrically averaged to be about 0.86 percent of the total factory cost with electric power at one cent per kw-hr. as against 0.29 percent for oil at 5 cents per gallon, or a difference of 0.0057 percent, which is about 6/1,000 of the cost of production. Hence we would equalize over-all factory costs in this case if we realize an advantage of only 6/1,000 over oil heating.

Whether that advantage comes from increased quality, in-

creased production, decreased floor space, better working conditions, ability to duplicate results, temperature control, uniformity of product, decrease in rejects, decrease in labor, or some other element entering into the total cost of production, matters not. Fortunately for electric heating, when these conditions are all taken at their increased value due to the electric process, the balance is in increasing numbers found to be on the side of the electric heat.

Lastly, some who have made a superficial study of electric heat do not appreciate the need of a resourceful furnace engineer for its successful application. Many of these are executives and engineers who insist on the last percent in efficiency for their motors, yet who accept heating equipment, such as furnaces of very low efficiency and, many times, doubtful economy of application. Many do not yet appreciate that a furnace must be designed with as much care and in such variety as machine tools, if you please. It has been assumed too often in the past that a furnace was simply a pile of bricks with a torch within it.

In other words, heat energy application in this country has in the not remote past been largely the composite result of promotion and advertisement, rather than scientific engineering. We have had fuel oil advocates, gas burning experts, powdered coal enthusiasts; other fuel promoters and perhaps electric furnace salesmen, but until recently we have lacked the competent furnace engineer familiar with all types of furnaces who could sit as court of appeals, and give unbiased decision regarding the true economic value of various furnace designs for specific applications. Let us profit, then, by the advice of the competent furnace engineer.

DISCUSSION.

Wirt S. Scott[1]: On page 137 under the item of "b," Mr. Collins says, "For the same rate of heat transfer the resistor temperature must be higher than for the unmuffled resistor or heat source." To my mind, it is not quite clear whether Mr. Collins means for the generation of a certain amount of heat,

[1] Mgr. Industrial Heating Section, Westinghouse Elec. & Mfg. Co., E. Pittsburgh, Pa.

or for the rate of transfer. If it is for the same amount of heat through a given area, his statement is correct.

But taking a furnace of 100 Kw. capacity, if that heat is all distributed along the sides of the furnace and it is muffled, then I agree with him that, if the resistor is exposed, located along the sides of the wall, it will be of a certain temperature, while if the resistor is muffled it will be of a higher temperature, assuming you are delivering the same capacity. But if you take that same capacity and distribute it over the four walls of the furnace, instead of the side walls only, then I contend you will have a lower element capacity than you will in the former case.

As to the manner of control of temperature, Mr. Collins again is fundamentally correct, but it will vary depending upon the application, as to whether you will obtain the over-shooting or under-shooting, as he points out. In furnaces where the work is placed in and heated for some considerable length of time, it has been my experience that a muffled furnace will give just as close control as an exposed element type. For very rapid heating, that may not be the case. However, I know of one particular case where brass was heat-treated in twenty minutes. This was during the war. And in one particular furnace, three and one-half million safety springs were turned out, requiring a temperature of 1,200° F. (649° C.) These springs came out without a single rejection, and without a single reheating of the material. We have other cases where work has been heat-treated in furnaces where very close temperature control is required. And in those cases where we have records, we have succeeded in obtaining a very uniform, accurate temperature control.

In other cases it may not be so. One case that recently came to our attention was in connection with the heating of bathtubs. We found in using the muffled type of furnace that the furnace walls would not liberate the heat fast enough; in other words, in order to get heat into the bathtub quickly enough, the element itself came up to a much higher temperature than the furnace walls. That was not objectionable on the part of the customer in this particular case, because in heating the bathtubs, a cold tub is placed in the furnace, and it is not an exact

temperature proposition. The workman watches the temperature of the tub itself and as soon as it reaches a certain temperature he pulls it out.

The limitation in that particular case was the ability to get heat into the furnace quickly. On longer heating propositions where you have a soaking period, such as in carburizing, annealing and work like that, the element temperature approaches the temperature of the furnace so closely that you can control either by the element or by the chamber, and to my mind it does not make much difference whether you use a muffled plate or the exposed element.

L. E. SAUNDERS[2]: We are interested, as users of electrical heating equipment, in the results accomplished, and in these discussions in which the efficiency of the heaters is described. What we are after are the results on our own wares.

I happen to be interested in a certain ceramic product. I have yet to find any one amongst these clever and efficient designers of apparatus who have that distinctly in mind. I suppose there is no place in industrial heating today where there is greater promise than in the electrical maturing of ceramic products.

We have not only the question of certain elevation of temperature and the maintenance of that temperature, but we have the question of the acceleration of temperature, and the decrease of temperature during the maturing of such ware. I hope that not only we who are interested in that subject, with our poor means of experimentation, but those who have more elaborate means, will enter this field and give attention to these questions, which are so vital to the ceramic industry. Mr. Collins and Mr. Scott seem to be in agreement on fundamentals; if they can only work out the details for us who use those fundamentals in practice, it will be advantageous to a great industry.

F. A. LIDBURY[3]: My experience as a user leads me to believe that the manufacturer of electric heating apparatus pays far more attention to the scientific and engineering bases of design, in an attempt to push to the limit the advantageous factors of

[2] Norton Co., Worcester, Mass.
[3] Works Mgr., Oldbury Electro-Chemical Co., Niagara Falls, N. Y.

electric heating, such as concentration of apparatus, economy of material, etc., than to the "laws of environment and psychology," particularly those relating to length of life. The position seems to be analogous to that of static transformer design of a decade or so ago, when the electrical manufacturers used to give us what a friend of mine described as "race-horse design for dray-horse work."

I have no doubt that the situation in this respect is clearing up, and will still further be cleared up, by the process of trying it out on the consumer. But even in lines of manufacture in which one would think the designers have now had lots of experience *via* the consumer, for example in immersion heaters, I have had recent experiences which indicate that insufficient attention is paid to the factor of durability in operation. While the difference in direct energy cost as compared with fuel is often negligible, as Mr. Collins has shown, the cost of maintenance, if it involves frequent replacements of expensive units, can become something considerable. I believe the comparative lack of attention paid to durability is doing more than any other one factor to hinder the more rapid application of electric heating apparatus.

F. J. Ryan[4]: I believe that the entire electric furnace or oven question has reached a point where those connected with it should decide as to whether the equipment will be hereafter manufactured wherever possible to meet the demands of the consumer, in place of being developed to meet only the ideas of the manufacturer. In other words, who is the "controlling factor?"

From a commercial standpoint it seems to me that we have passed sufficiently out of the experimental stage, and the fundamentals have been sufficiently established, in order that we can consider the question from the viewpoint of consumption of product, and therefore develop future equipments along the lines of the ideas of the consumer.

True, the manufacturer of electric apparatus deserved considerable praise and recognition in the way he has assisted in the development of the problem. However, the real, true and important assistance has been that which has been given by the

[4] F. J. Ryan Co., Philadelphia, Pa.

consumer. While a few incidental and outlying cases might be cited where equipment is entirely the product of the manufacturer, he may or may not be the electrical designer. In the majority of cases, at least those which have come to my attention during my experience in direct sales work on electric furnace products of all kinds, the product is the result of willingness on the part of the consumer to assume the burden and cost of experimentation and first testing of furnace equipment.

I believe, therefore, that as the consumer has been willing to co-operate and assume the bulk of the expense, because practically all of the money which is today invested in the electric furnace field represents profits from equipment purchased by the consumer, he should be recognized, and his opinions should have our close attention. Our research development should be along lines which will assist him in making the electric furnace a practical working unit, competing directly with other fuels, at least in ultimate results, if not in cost of consumed heat.

I can cite a particular case that came to my attention—that of the Gleason Works of Rochester. They had a particular type of gear heat treatment upon which they wished to apply the electric furnace, and they had certain general ideas as to the way they would like the furnace to operate. This suggestion was submitted to a number of electrical organizations and furnace managements, who refused to submit proposals or designs, stating that the arrangement would not work out, and it was incorrect in accordance with the fundamentals of present practice. As a result the Gleason Company proceeded to manufacture a furnace, which proved highly satisfactory and showed an entirely new way of continuous operation.

There is so much to be learned and so many possibilities of improvement, especially towards cheapening the product, which is now one of the chief stumbling-blocks in its progress, that it seems to me we are wasting too much time in advocating impractical and special types of applications. The question of the exposed or the blanketed resistor, or the type of refractories, and the question of control are purely questions of the specific operation. I do not believe that manufacturers

should take any determined stand upon whether the treatment or the input should be this or that.

When it comes to the question of treatment or time element, the customer or consumer can show us the way. He has worked this out through years of practice, and I believe the electric furnace will take its place more rapidly if we take his conditions and apply them to a possible electric heating unit. We must meet the conditions and the demands of the manufacturer. If we do not, the control of the future of electric heat will pass out of the hands of those who are giving it their attention, and into the hands of individual organizations.

Briefly, my advocation is the tendency of this Society to seek out papers and knowledge on the requirements of the manufacturer or consumer, and try to assist in both research and practical ways of meeting his ideas. I believe that in doing so we would assist in keeping up the enthusiasm of this particular electric furnace section, and would be rewarded by a strong backing from outside interested laymen.

E. F. Collins: First of all, I think you have a much more narrow conception than I of the term "heating engineer." I regard a man who is solely a designing engineer of electric heating equipment and nothing more as filling about ten percent of the heating engineer's requirements. I believe the application of the device to industrial processes is about nine times as important as its design, and I have said, from the very beginning, when I was asked to engineer the development of electrical heating equipment, that I could only hope for success with the understanding that I should also do the necessary application engineering.

It has been my conception from the beginning, that I could not hand over to a customer proper heating equipment without previous consultation, and without having made a study of conditions where this apparatus was to work, and the peculiar conditions or environment under which the heating device must perform. I have looked at industrial heating as a problem entirely different from domestic heating, and in that way I have always practiced it.

I do not think we want to give praise to the manufacturer or to the consumer alone, that is, to either separately, or to

try to estimate their efforts in that way. We will never get anywhere unless both co-operate, and co-operate to their fullest extent. Wherever industrial electric heating cannot be applied with real advantage to the user as well as to the electric manufacturer, let us not undertake it. If there has been anything that I fought hard against in my experience in this work, it has been to keep an over-credulous user from taking up and trying to apply electric heating equipment where it cannot at present show economy. There are doubtful cases where it seems it will never be as efficient as other methods of heating.

Therefore, I am heartily and enthusiastically an advocate of the most careful study of the whole proposition before we attempt to apply electric heat to it. If the proposition does not, as an "over-all" proposition, decidedly show that it is better economy, true and real economy, to go to electric heating, then I urge you to forget all about it.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 21, 1922, President Schlueder-berg in the Chair.

PRINCIPLES OF HIGH TEMPERATURE FURNACE DESIGN.[1]

By E. L. Smalley,[2]

Abstract.

The best electric furnaces, judged from the view points of highest quality of products, lowest cost of operation and maintenance, and greatest safety in operation at high temperatures, must have these attributes: Muffled type where best suited to the process. Exposed element or radiant form only when best adapted to a process. Must have elements of sufficient number for cheap renewal. Elements must be readily and easily renewable. Coils must be fully supported, and yet free for expansion. Refractory parts must be thoroughly supported, but free for expansion. No internal connections of coils should be tolerated. Terminal sizes should be larger than the element size. Source of heat must be uniformly distributed. Size of furnace must be governed by the charge. Placement of elements should not control the furnace size. Thermal efficiency should be a controlling feature in decision. Transverse section of heating elements should be round. Exposed elements should preferably be in corrugated grooves. Elements should not be chosen to suit a voltage. Total weight of heating element should be high in proportion to the weight of the charge. Efficiency of heat insulation must be adapted to the work to be performed. All of these characteristics, when properly combined with one another, will make the furnace most successful.

Electric furnace designers should profit by the experiences of fuel furnace builders. The chief aim and ambition of fuel furnace

[1] Limited to the discussion of electric furnaces having metallic resistor elements and to be operated at temperatures not in excess of 2000° F. (1093° C.). Manuscript received August 8, 1922.

[2] Manager, Electric Heating Apparatus Co., Newark, N. J.

builders have been to attain a furnace which will give a uniform temperature throughout the entire furnace chamber. This is perhaps the chief requirement of any furnace, irrespective of whether it be fuel or electric. It certainly is the most desirable characteristic to secure in an electric furnace.

The designers of fuel furnaces have gone through a tedious course of modifying the designs to secure uniformity of temperature. In the case of gas or oil furnaces they have increased the number and changed the distribution of burners with this aim in view. They have tried under-fired furnaces, over-fired furnaces and furnaces with burners impinging flames only through the side wall. They have changed to modifications of these types so that by means of flues they could better distribute the heat around all sides of the furnace chamber.

They have always been handicapped by the fact that the greatest temperature exists at the point of greatest combustion. This combustion temperature, oftentimes in excess of the temperature they wish to utilize, must be decreased at the point of application to the work to be performed.

The electric furnace designer has the advantage of all the experience of the fuel furnace designers, but in the case of the electric furnace the heat is developed solely within the furnace chamber, and the electric furnace designer, therefore, has the marked advantage of being able to distribute his heat uniformly as needed for the work to be performed. Unlike fuel furnaces, which oftentimes must be increased in chamber size so that the work to be heated could be far removed from excessively hot spots of the fuel furnace, the electric heat may be so distributed that this is not necessary.

Furnaces may be either of the exposed element type, or the elements may be covered with refractory plates; the latter being so-called "muffle plates" and the furnace a muffled furnace. The choice lies with the designer, but due consideration should be given to the results attained. In a muffled type of furnace annealing glassware, goblets were placed in parts of the furnace within 1.5 inches (3.8 cm.) from the source of heat. With the same current density, exposed elements would have melted the goblets. The current density of a heating element in a muffled furnace and the

current density in the heating elements in an exposed element furnace must both be made to suit the required conditions. Muffled type of furnaces have certain advantages regarding the exclusion of a large portion of the oxidizing atmosphere of the furnace, and unquestionably the elements are, therefore, protected from oxidation to a marked degree. A muffled furnace is an insurance for the operator against contact with the furnace coils. In some processes, owing to its being the only method of correct application, the muffled type of heating element is absolutely essential to the success of the equipment.

It is wise to have the heating circuits of any furnace divided into several coils. This will lessen the cost of maintenance, as it cheapens the cost of renewal of any one burnout. It makes easier the replacement of the element by the operator. It lowers the amount of capital tied up in spare or extra coils on hand for emergency service.

The weight of unsupported portions of elements should not be excessive. Proper support of elements will prevent distortion of elements at the high temperatures they are sometimes called upon to sustain. Such distortion may cause the necessity of "crimping" the elements to bring them back to their original overall length. Crimping or changing the original form weakens the element for subsequent expansion and contraction, and may result in short circuiting of the elements. It is a practice that should be avoided.

Allowance for expansion and contraction of refractory parts in the furnace must be provided. The expansion and contraction of the heating elements in the heating and cooling periods of the furnace must be arranged for, and during such expansion and contraction the original form of the heating element must be maintained.

All connections of the power source to the furnace circuits should be made outside the furnace. Where the terminals of heating coils extend through furnace walls the cross-sectional area of the terminals should be increased above that of the main body of the heating element, as otherwise there would be local overheating in the terminals. In placing heating elements in the bottom of furnace chambers thorough protection against contact with foreign substances should be provided. This has been accomplished

in a large number of instances by means of cast non-oxidizing floor or cover plates. These floor or cover plates may be provided with lock-joints to exclude foreign substances and still provide means for expansion and contraction of the floor plates. The structure under such floor or cover plates must be such that the bottom coils are free to expand and contract, same as any other coils, and they must be kept in proper alignment.

An electric furnace is not successful simply because it is electric. Marked errors in design may exist which will be detrimental to the most efficient results. An electric furnace can have overheated zones; the same furnace can also have low temperature zones. Uniform temperature depends entirely upon the uniform distribution of the s o u r c e of heat. Heat rays follow the same laws as light rays. In order to have the same density, or intensity, of light on all sides of an object, the s o u r c e must be from all sides. So it is with heat rays. The uniform distribution of heat in the electric furnace should not be sacrificed to the convenience of the method of mounting the heating elements.

The design of the heating element must necessarily be one that can be readily mounted on any wall and in the floor of the furnace chamber. Even car-bottom furnaces have been successfully operated, wherein some of the heating elements are located on the floor of the car. Power connections are made with the customary type of third rail contact shoes.

The temperature will not be uniform unless the heat source is uniformly distributed in the heating chamber.

It is a grievous fault of some electric furnace designers that they design the height and width of the chamber to suit the application of the heating element. Of course, the size of the charge to be placed in the furnace should be the sole factor in determining the furnace dimensions. Any enlargement of the furnace to suit the elements, invariably results in a greater radiation loss, and consequently a lower thermal efficiency. A difference of f i v e percent in the efficiency of a two hundred kilowatt furnace amounts to $748.80 in one year, with current at one cent per kilowatt hour and the furnace operated 144 hours each week. Yet a reduction of t e n percent in efficiency can easily be made by a false choice of size. Weigh furnaces, in part, by their efficiencies.

Consider three furnaces all having the same full load or kilowatt rating, and each having exactly the same radiation losses, and therefore, the same thermal efficiency. One hundred kilowatts per hour can be released in a furnace heated by a single arc, and likewise 100 kilowatts per hour can be released in another furnace where the total source of heat is from the side walls. A third furnace may be designed so that the 100 kilowatts per hour is released uniformly from the entire surface of the interior walls of the furnace. In the first instance, the temperature of the electric arc may be excessive for the work to be performed. Experience shows that the heat tapers from that of the electric arc to the saturation temperature resulting at points remote from the arc. The second instance, of a furnace having only side wall elements is a modification of the first furnace, but having its source of heat somewhat more widely distributed. In the third furnace, the same amount of heat obviously is delivered from a greater area and, therefore, more uniformly saturates the entire furnace chamber.

The single arc furnace is comparable to a fuel furnace of one burner; the side element furnace to a furnace having side wall burners with no means of distributing the excessive heat at the point of combustion or at the source of heat. The third furnace exactly approaches the ultimate aim of all fuel or electric furnace designers.

Is this theory of heat requiring a source distribution for uniform temperature, actual or only theoretical? A committee of research engineers in studying the types of electric furnaces offered to their company for certain specified work, reported, in part, as follows pertaining to an electric furnace having side wall elements, and to a second furnace having the furnace chamber completely surrounded by source of heat.

"Assuming that the same quantity of heat is to be delivered within the furnace within a given time, it seems possible to draw a very interesting conclusion as to the two types of furnaces. Radiation takes place by virtue of difference in temperature between the bodies delivering and receiving the heat; as a matter of fact, in proportion to the difference of the fourth powers of the absolute temperature. In the one furnace we have as effective

radiating surface practically the entire inner surface of the furnace, which is approximately 220 sq. ft. (19.8 sq. m.). In the second furnace we have as the initial radiating surface the sum of the sides bearing resistors, which is approximately 95 sq. ft. (8.55 sq. m.).

"By the term 'effective radiating surface' we mean the area of the side of the furnace actually covered by the resistor as a whole, it being our impression that the resistor must be considered as an assembly, and not as individual ribbons or wires.

"The conclusion which we draw is that if a given quantity of heat is to be delivered from each of two radiating surfaces to bodies of the same temperature, and one effective radiating surface is larger than the other, the temperature of the larger radiating surface will be lower than the temperature of the smaller; in other words, to radiate a given amount of heat the temperature of the radiating surface varies inversely with the area of that surface."

The conclusion reached by the committee of research engineers has been proved correct by the temperatures secured in various electric furnaces.

A certain electric furnace in Connecticut has no bottom nor top heating elements. The furnace is used for annealing castings. Temperature control is secured by a Leeds & Northrup automatic control, set at 1500° F. (816° C.). The cycle of operation is of several hours duration, so that a long period should saturate the load to uniformity, provided the source of heat was not opposed to the laws of light and heat. The source of heat does not surround the charge.

Castings are placed on two trays, one above the other and the temperatures reached in the heating zone have been reported by the operator as follows:

Top of top tray	1454°F. (790°C.)
Bottom of top tray	1382°F. (750°C.)
Top of bottom tray	1346°F. (730°C.)
Bottom of bottom tray	1310°F. (710°C.)

Note that the variation in the charge is 144° F. (62° C.). Since the temperature of the charge varies 144° F., it is apparent that the element temperature is above the set control temperature of 1500° F. (816° C.), or at least 200° F. (93° C.) above the lowest

temperature of the charge. In an electric furnace of the exposed element type, with heating elements completely surrounding the charge, bath tubs are being coated with vitreous enamel at 1750° F. (954° C.). Element temperatures are taken by means of small diameter pyrometer couple elements wired in direct contact with the heating elements. The side and top elements with full power applied show 1850° F. (1010° C.) and the bottom elements under cast non-oxidizing floor plates 1920° F. (1049° C.) a difference of only 170° F. (77° C.) maximum between the hottest element temperature and the temperature of the charge, compared with at least 200° F. (93° C.) with the side element furnace.

In contrast to the variation in temperatures of the electric furnace in Connecticut a report has been given regarding another electric furnace, having heating elements completely surrounding the furnace chamber. A glass manufacturer of West Virginia writes as follows:

"We were able to maintain a uniform heat throughout the furnace, both top and bottom, and throughout its length to a range of 1.5° plus or minus. The furnace was operated to a temperature of 1020° F. (549° C.) for the purpose of annealing glass ware. Because of the uniform temperature we were able to have ware so unvarying in quality of anneal as to free us from all anxiety."

In still another furnace having no top nor bottom heating elements 1000 pounds (455 kg.) of brass tubes were placed, to be satuated to a uniform temperature of 1200° F. (649° C.). The consulting engineer who instigated such test reported that it took five hours and fifteen minutes to saturate the tubes so that the pyrometer couple at the bottom center finally read the same temperature as other couples placed in the center of the mass of tubes, at the top of the tubes, and at each side of the mass of tubes.

A second test in the same furnace was conducted similarly, but the stack of tubes was elevated from the floor of the furnace chamber, it being the intention more freely to radiate and convey heat to the under side of the tubes. In this test, in the same furnace as the first test, it required 2 hours 25 minutes to secure uniformity of saturation at 1200° F. (649° C.).

Another test was conducted using a similar mass of tubes placed in another electric furnace, in which heating elements were uni-

formly distributed on top, bottom and two sides of the furnace chamber. Couples were placed in the same locations as in the first test. Complete saturation was attained in 28 minutes. From the above facts it is conclusively proved that the source of electric heat should be distributed uniformly in order to secure uniform heat irrespective of time cycle of heating.

The form or shape of the heating element has a direct bearing on the life of the resistor element. The choice lies between round elements or flat, so-called, ribbon elements. It can be shown mathematically that the greater area of the ribbon element per weight of section is free to dissipate more rapidly its generated heat than the round element. That is true only in so far as the comparison of elements is concerned, without their relation or adaptability to electric furnace construction. The round element as a furnace element is more practical, and will give greater life than the ribbon element in electric furnace construction.

There is no method of applying ribbon elements so as to take advantage of the greater releasing heat surface. When placed along the walls of a furnace, recourse is had to only two methods of application. In one the flat faces of the ribbon are perpendicular to the wall, and in another application the flat face of the ribbon is parallel with the wall. In the perpendicular position the wide faces of any one strand of the element is directly opposed to the wide radiation surface of the adjacent strand. The heat released by radiation, therefore, reflects the same as light waves from one face to another until a built up temperature exists, considerably in excess of the furnace temperature.

The heat waves then are forced both to the adjacent side wall and to the furnace chamber. The heat waves directed in such manner to the wall of the furnace tend to saturate the wall of the furnace considerably above the normal furnace chamber. Such heat cannot be freely released until the current is completely cut off or lowered in the furnace elements, because the greater heat transmission is from the hotter to the cooler body.

If the wide face of the ribbon is parallel to the adjacent wall a built-up temperature will exist, because the heat released from the face of the ribbon nearest the wall, cannot become effective until a temperature exists greater than the furnace temperature, or greater than the charge receiving heat.

The round element, on the other hand, can be placed in corrugations of the furnace wall, so that the generated heat is directly reflected from the groove of the wall face. The surface of these corrugations can be shaped exactly similar to search light reflectors, and actually throw the reflected heat to the furnace chamber and charge. There is, therefore, no built-up temperature in the resistor element. As the convex tops of the corrugations may extend considerably beyond the heating elements, marked advantages will be secured. The corrugations protect the elements from short circuiting by foreign substances as the elements are in effect imbedded below the wall surface. The corrugations keep the elements in perfect alignment. The face of the wall is free at all times to release stored up heat, and the corrugated surface may add as much as fifty percent to the radiating surface of the wall without enlarging the furnace chamber.

The round element is of greater strength than the ribbon element of equal weight, so that the round element is more susceptible of being permanently formed and kept in original proper alignment.

It is susceptible of easy proof that the round element, under equal furnace conditions will outlast in life the ribbon element. Barring mishaps or accidents, the sole cause of disintegration of a furnace element is due to oxidation. Fortunately, at the present time there are available elements of alloys or metals that will give surprising life in service. However, there is a gradual disintegration by oxidation; no one will claim perpetual life in such use.

Compare two typical element sections. The cross-section area of No. 1 round wire is 0.0656 sq. in. (0.426 sq. cm.). A flat or ribbon element of No. 11 B. & S. gauge, 0.091 in. (0.231 cm.) thickness, and having the same area as the No. 1 wire, would be 0.7209 in. (1.831 cm.) wide. The circumference of No. 1 wire equals 0.9079 in. (2.306 cm.). The perimeter of the ribbon element equals 1.6238 in. (4.124 cm.). Therefore, the ribbon element has 0.7159 sq. in. more area per inch of length or 78.85 percent more area exposed to oxidation than No. 1 round wire of the same weight.

Assume that the No. 1 round wire and the ribbon element, 0.7209 in. wide by 0.091 in. thick, oxidized to the same depth of

0.005 in. of oxidation. The No. 1 wire would be decreased to 0.279 in. diameter, an area of 0.0612 sq. in. or a reduction of only 6.71 percent of area. The ribbon would be reduced to 0.7109 in. wide by 0.081 in. thick equal to 0.0576 sq. in. of area or a reduction of 12.19 percent.

In a furnace operating 2½ years at temperatures varying from 1200° F. (649° C.) up to 1650° F. (899° C), it was found by micrometer measurement that the original diameter of the elements 0.204 in. diameter had been reduced to 0.201 in. This furnace had elements surrounding the furnace chamber. If the same furnace had had the elements only in the side of the furnace chamber the decrease by oxidation would have been greater on account of the higher temperature that would have existed in the elements to deliver the same quantity of heat.

Increasing the diameter of a round wire so that the weight is doubled, causes an increase of only 41.6 percent of oxidizing area. A No. 1 wire is double the weight of a No. 4 wire, yet 123.7 amperes in a No. 1 wire will release as much heat as 87.5 amperes in a No. 4 wire; or, increasing the weight per foot of round wire 100 percent requires only 47.2 percent increase of amperes or current density to produce the same quantity of heat. As the weight of the wire has been doubled, it is obvious that the temperature of the source of heat must be lower.

From the foregoing, it is evident that the relation of the weight of the elements to the work to be performed is of vital importance.

The cross-sectional area of the weight of the element should never be sacrificed so as to be used on any line voltage available, but rather the furnace voltage should be made suitable to the furnace element requirements. The weight of the element should be kept constant, irrespective of whether the line voltage be 110 or 220 or 440 volts or higher. It being true that a certain total weight of element is most advisable for performing a certain piece of work, then it becomes impossible to decrease the weight of that element for adoption of any line voltage without the sacrifice of the ultimate life and efficiency of the furnace.

Exposed element furnaces especially should have low voltage as a safeguard to the operator. Some furnaces, owing to their size, might have their elements figured for a line voltage, but it is of doubtful expediency to operate any exposed element furnace on

any voltage that might prove harmful to the operator. It is far more advisable to reduce the furnace voltage to a safety point. The low voltage furnaces are unquestionably advantageous, because the dielectric strength of refractory materials at high temperatures is questionable.

The relation of the weight of the heating element to the work to be performed is of just as much importance as the current density of any element is to the life of the resistor element. An increase of the total weight of element in a furnace permits of the release of the same quantity of heat from the source at lower temperature. Likewise, the temperature of the heating element is lowered in direct proportion to the increase of the weight of the element to the work performed. It is obvious that a required quantity of heat can be released from any given total weight of heating element, so long as the element retains its form. Ten pounds of heating element may be made to operate at a sufficient temperature to release the same amount of heat as 100 pounds of heating element. It is obvious that under these conditions the temperature of the 100 pounds of heating element will be much lower, in fact almost inversely proportional to the weight of the element. The furnace designer, therefore, should not undertake to decrease the weight of the element for any reason. If he does it will be to the detriment of the life of the furnace element.

No set rule, however, can be established governing the relation of the weight of element to the current density of the element. The current density required is controlled, in part, by the thermal efficiency of the furnace, and the thermal efficiency is a matter of mechanical design in combination with proper selection of the heat insulating material. For example, if an electric furnace has to deliver 50 kilowatts per hour of effective heat and the radiation loss is 10 kilowatts per hour, the element of that furnace will require lower current density and consequently operate at a lower temperature than in another furnace designed for the same work and having the same weight of heating element, but having 30 kilowatts per hour loss. Any difference of thermal efficiency, therefore, has to be accounted for by a rise of temperature in the element to overcome the excessive radiation loss.

The heat insulation, in addition to controlling the current characteristic of the heating element somewhat, also actually controls

the result required. Certain desired heating cycles, such as one of moderately quick heating and quick cooling, may be defeated in a furnace by an excessive amount of heat insulation.

The thermal efficiencies of electric furnaces, such as are offered on the market at the present day for operating temperatures of 1600° F. (871° C.), vary from 50 to 90 percent thermal efficiency. A furnace in Ohio, having elements on top, bottom and two sides of the furnace chamber is being operated continuously at 1600° F. (870° C.) and shows a thermal efficiency of 88.9 percent. The thermal efficiency of a furnace may establish its success or failure.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 21, 1922, President Schlueder-berg in the Chair.

SOME ELECTRICAL PROPERTIES OF ALLOYS AT HIGH TEMPERATURES.[1]

By M. A. Hunter[2] and A. Jones[3]

INTRODUCTION.

A heating unit is fundamentally a machine for the conversion of electrical into heat energy. The energy converted in any given case is represented by the well known formula $I^2 R t$. It is evident then that the energy transformed is primarily dependent on the resistance of the wire used in the unit at the temperature of its operation.

A review of the literature on the subject of metals and alloys discloses a considerable amount of information on the specific resistances of these materials, and also on their temperature coefficients between room temperature and 100° C., but information on these points over the higher ranges of temperature is meager or entirely lacking. In an attempt to find the resistance of any proposed unit at temperatures in excess of this low range, the manufacturer is compelled to use the data which are available for the low range of temperature, and by an extrapolation to calculate the resistance of the unit at the temperature of the proposed operation. This of course involves the assumption that the temperature coefficient of the metal or alloy used is uniform throughout the whole range of operating temperatures—an assumption which has been found to be very far from the truth.

The present paper is an attempt to clarify this situation. The specific resistances of a number of the metals and alloys, which are in commercial use, have been determined over the range from room temperature to 1,000° C. With the information which is here available it will no longer be necessary for the manufacturer

[1] Manuscript received August 9, 1922.

[2] Rensselaer Polytechnic Institute. Director of Research Driver-Harris Co.

[3] Rensselear Polytechnic Institute, Troy, N. Y.

of heating units to base his calculation of the resistance of any heating unit at high temperature on data which are insufficient and in many cases wrong.

MATERIALS USED IN HEATING UNITS.

The wires or strips of material which are used in the construction of heating units have the metal nickel as their essential base. Pure nickel has usually been considered an unsatisfactory material, by reason of its low specific resistance. It does not lend itself to the production of the maximum quantity of heat energy with the minimum amount of material or in the minimum space. The same objection is urged and with equal truth against the commercial grades of nickel (grades A, C, and D), which are available.

The specific resistance of nickel can be readily raised by the addition of metals which form solid solutions with it. This can be done commercially in an effective way by the addition of copper or of iron. The addition of either of these metals will increase materially the specific resistance of the metal, and will at the same time cheapen the alloy. It must not be forgotten however that the temperature coefficient of resistance of the resulting alloy is always materially lower than that of the pure metals—a fact which at high temperatures offsets to a considerable degree the initially high resistance of the alloy.

All of these alloys, however, have a limited use. Since the units in which they are used are run in air, the metal is always exposed to oxidation, the evil effects of which are increased as the temperature rises. None of these materials, with the exception perhaps of nickel itself, can be run at temperatures greatly in excess of 500° C.

For the range of temperatures between 500° and 1,100° C., alloys of nickel and chromium, of iron, chromium, and nickel, and of iron and chromium are available. All of these alloys belong to the class of solid solutions, have exceedingly high specific resistances at room temperatures, but have low temperature coefficients which, however, are in no case uniform throughout the whole range. In addition they possess in varying degrees, according to their composition, the property of resisting oxidation in air upon continued exposure.

The alloys investigated in this report fall naturally into two classes.

A. *Materials available for heating units up to* 500°C.

	Material	Trade Names
1.	Nickel	Electrolytic; Grade A; Grade C; Grade D
2.	Copper-Nickel	Monel; Advance
3.	Iron-Nickel	Alloy No. 141; Alloy No. 193

B. *Materials available for heating units in excess of* 500°C.

	Material	Trade Names
1.	Nickel-Chromium	Nichrome IV; Nichrome III
2.	Nickel-Iron-Chromium	Nichrome; Nichrome II
3.	Iron-Chromium	

TABLE I.

Analysis of Materials.

	Ni	Cu	Fe	C	Mn	Si	Cr
Grade A Nickel	98.85	0.24	0.65	0.08	0.08	0.03	....
Grade C Nickel	96.15	0.40	0.89	0.22	2.10	0.18	....
Grade D Nickel	94.10	0.16	0.74	0.08	4.75	0.13	....
Monel	68.10	27.66	2.40	0.16	1.50	0.11	....
Advance	44.00	54.00	0.45	....	1.16	....	....
Alloy No. 141..	69.33	0.16	28.86	0.22	1.30	0.13	....
Alloy No. 193..	30.00	....	67.00	....	1.00	....	2.00

Group A. Materials available for low Temperature range.

In Tables II and III will be found the electrical characteristics of various grades of commercial nickel, of two alloys of copper and nickel, and two alloys of iron and nickel. The exact analyses of the wires used are given wherever possible. In two cases, only an approximate analysis was available.

The variation in the resistance of each material with temperature is given in Table II. The figures in each column represent the resistance at the indicated temperature of a length of wire having one ohm resistance at 20° C. In the actual measurement the wire was first carried to the maximum temperature at which measurements were required. After cooling to room temperature

TABLE II.

Variation in Resistance of Various Materials.

Temp. °C.	Electrolytic Nickel	Grade A Nickel	Grade C Nickel	Grade D Nickel	Monel	Advance	Alloy No. 141	Alloy No. 193
20	1.000	1.00	1.00	1.00	1.000	1.000	1.000	1.000
100	1.45	1.43	1.36	1.29	1.157	0.9992	1.34	1.093
200	2.07	2.06	1.90	1.68	1.217	0.9995	1.79	1.198
300	2.86	2.83	2.58	2.10	1.254	1.002	2.28	1.292
400	3.69	3.52	3.02	2.31	1.294	1.006	2.82	1.365
500	4.00	3.87	3.26	2.46	1.339	1.020	3.46	1.425
600	4.31	4.15	3.49	2.62	1.384	1.039	3.94	1.472
700	4.62	4.44	3.73	2.78	1.434	....	4.03	1.504
800	4.93	4.73	3.96	2.94	1.488	....	4.11	1.538
900	5.24	5.04	4.22	3.13	1.550	....	4.20	1.585
1000	5.64	5.38	4.50	3.32	1.626	....	4.32	....

TABLE III.

Specific Resistances of Various Materials.

In ohms/mil foot

°C. Temp.	Electrolytic Nickel	Grade A Nickel	Grade C Nickel	Grade D Nickel	Monel	Advance	Alloy No. 141	Alloy No. 193
20	58.6	64	84	117	268	290	182	530
100	85	92	115	151	310	289	244	579
200	120	132	160	197	326	289	326	635
300	161	182	217	246	338	291	415	685
400	216	226	254	270	347	292	513	723
500	238	248	275	288	359	296	630	755
600	255	266	294	307	371	301	717	780
700	271	285	304	325	384	....	734	797
800	289	303	334	343	399	....	748	815
900	307	323	356	366	416	....	764	840
1000	331	345	379	389	437	....	786	....

again, a second set of measurements were made on the wire. By this means the wire was stabilized over the range desired.

In Table III the specific resistances are calculated on the basis of the results shown in Table II.

A review of the results shown in Table III allows us to compare the specific resistances of the various materials at any given temperature.

The various grades of nickel, by reason of their high temperature coefficients, have values for specific resistance at 500° C. much greater than would be expected from their initial resistances at 20° C. The break in the temperature-resistance curves for each

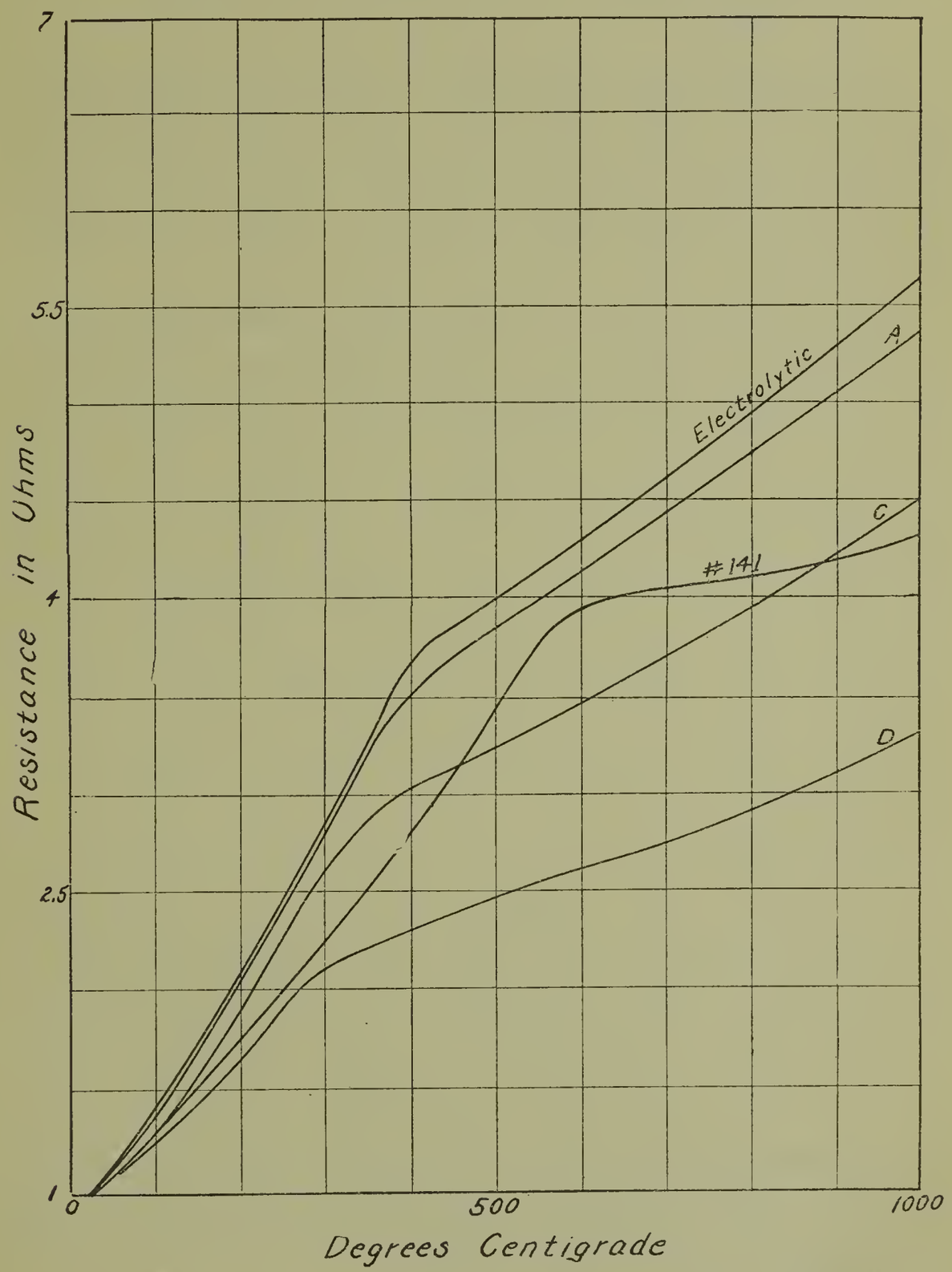


FIG. 1. Four grades of Commercial Nickel

material represents the transformation point of the material. The approximate temperatures of these transformations are as follows:

Grade of Nickel	Temperature, °C.
Electrolytic	360
Grade A	350
Grade C	320
Grade D	275

The resistance-temperature curve of monel changes direction sharply at 93° C., the transformation point of the material. Below this temperature monel has a high temperature coefficient, while above it the temperature coefficient is quite low. At 500° C. its specific resistance is not, therefore, as high as might have been expected.

The copper-nickel alloys (Cu 55:Ni 45), of which Advance wire is taken as a type, stand in a class by themselves. The high content of copper in the material renders the wire much more susceptible to oxidation than is either nickel or monel. These alloys are entirely satisfactory for units which are to run at constant current up to temperatures of 300° C. By reason of a low temperature coefficient, the resistance of the wire remains practically constant over this range. The resistance-temperature curve changes sharply upwards at about 400° C. This is not due to a magnetic transformation point in the material, since Advance is already non-magnetic at room temperature. Neither is it due to excessive oxidation at the temperatures indicated, since the wire, after being heated, returns on cooling to its initial resistance.

The two alloys of iron and nickel of which alloy No. 141 (Ni 70:Fe 30) and Alloy No. 193 (Ni 30:Fe 70) are taken as types have at 500° C. specific resistances which are far in excess of any of the other materials in the table. The transformation points of the materials are both in the neighborhood of 600° C., so that both materials retain their high initial temperature coefficient throughout the whole range considered. Alloy No. 141 has at 20° C. a low specific resistance but its temperature coefficient is of the order of commercial nickel. In consequence, at 500° C. it has a very high specific resistance for a material of its class. On the other hand, alloy No. 193 has a high initial specific resistance with a much lower temperature coefficient.

From the point of view of resistance to oxidation it would

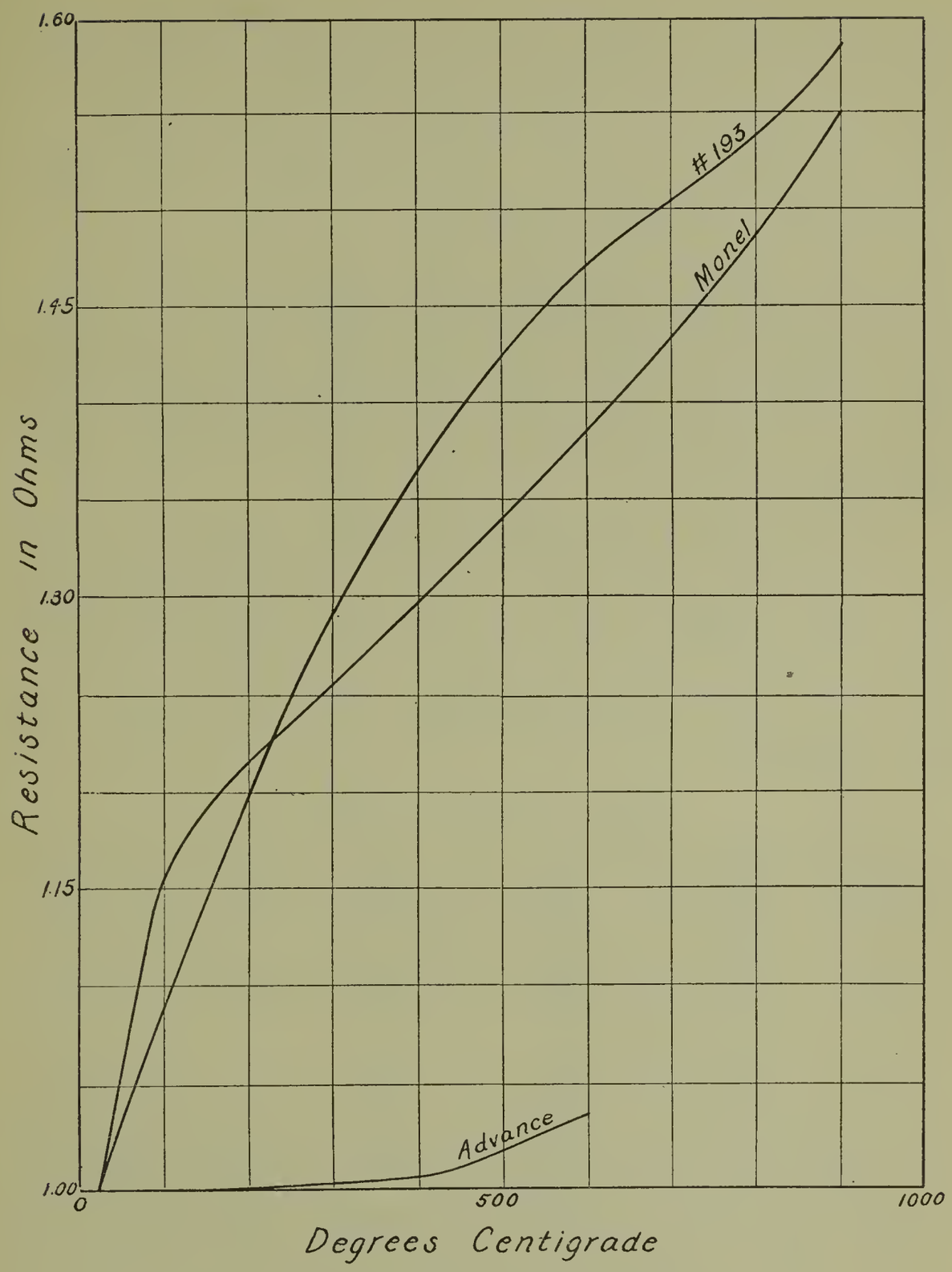


FIG. 2. Copper-Nickel and Iron-Nickel alloys

naturally be expected that alloy No. 141, containing 70 percent of nickel would withstand oxidation to a greater extent than alloy 193, containing 30 percent of nickel. The resistance to oxidation of this latter alloy is materially increased by the addition of chromium up to 2 percent. An alloy of this composition finds

extensive use at the present time in many household appliances, which run at temperatures at or below a dull red heat. This material is cheap, has a high specific resistance, and resists oxidation sufficiently at the temperatures demanded. For more strenuous service at higher temperatures alloy No. 141 will be found to be a satisfactory substitute.

Group B. Materials Available for High Temperatures.

The second group includes all those alloys which are essentially combinations of nickel, iron and chromium in various proportions. Most of these alloys have been worked under a patent granted to Marsh in February, 1906, which will expire next year (February, 1923).

These alloys are remarkable in that they possess very high specific resistances and resist oxidation at high temperatures to a very marked degree. While their specific resistances and temperature coefficients at room temperature have been known from the beginning, no exact information on their specific resistances and temperature coefficients at high temperatures has as yet been disclosed.

Nickel-Chromium Alloys.

The simplest combination in this group is the binary alloy of nickel and chromium. Alloys containing as high as 25 and 30 percent of chromium have been made. It is commercially practicable to make alloys containing 15 and 20 percent of chromium. An alloy containing more than 20 percent of chromium is exceedingly hard to draw into wire.

In general, it may be said that the resistance to oxidation bears a direct relation to the amount of chromium in the wire. This is certainly true for chromium contents up to 20 percent and probably holds also for higher percentages. For temperatures around 1,000° C. alloys of the Nichrome III class, containing 15 percent of chromium have given good service. For the higher range between 1,000° C. and 1,100° C. alloys of the Nichrome IV class containing 20 percent of chromium are necessary. While these alloys may be used for short periods at temperatures above 1,100° C., their life is under these conditions exceedingly short.

The specific resistances and temperature coefficients of various alloys containing nickel and chromium are given in Table IV.

TABLE IV.

Variation in Resistance of Alloys of Nickel and Chromium.

NICHROME III.

Temp. °C.	No. 5	No. 6	No. 1	No. 4	No. 11	No. 10	No. 13	Mean
20	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
300	1.055	1.034	1.047	1.037	1.057	1.040	1.039	1.043
400	1.066	1.047	1.063	1.051	1.068	1.051	1.053	1.056
500	1.073	1.060	1.071	1.063	1.075	1.060	1.063	1.066
600	1.071	1.058	1.074	1.061	1.074	1.058	1.062	1.065
700	1.072	1.060	1.077	1.062	1.077	1.063	1.065	1.068
800	1.074	1.066	1.088	1.068	1.086	1.072	1.073	1.075
900	1.082	1.076	1.100	1.094	1.096	1.083	1.083	1.088
1000	1.097	1.090	1.118	1.104	1.112	1.098	1.099	1.103
Percent chromium	14.10	14.45	15.40	15.60	15.70	15.80	16.20	....
Resist, in ohms/mil foot at room temp.	604	604	564	567	599	595	553	....

NICHROME IV.

Temp. °C.				
20	1.000	1.000	1.000	1.000
300	1.034	1.027	1.026	1.025
400	1.046	1.036	1.032	1.038
500	1.060	1.045	1.041	1.042
600	1.055	1.036	1.034	1.032
700	1.056	1.032	1.030	1.028
800	1.063	1.033	1.031	1.028
900	1.074	1.038	1.035	1.030
1000	1.090	1.049	1.046	1.040
Percent chromium	17.47	18.18	18.70	18.95
Resist. in ohms/mil foot at room temp.	575	620	629	633

The results set forth in Table IV indicate an interesting peculiarity which seems to be inherent in all nickel-chromium wires. In the case of the Nichrome III alloys (around 15 per-cent chromium) the resistance-temperature curve rises at a uniform rate up to 500° C. From 500° C. to 700° C. the curve runs practically parallel to the temperature axis, indicating a low

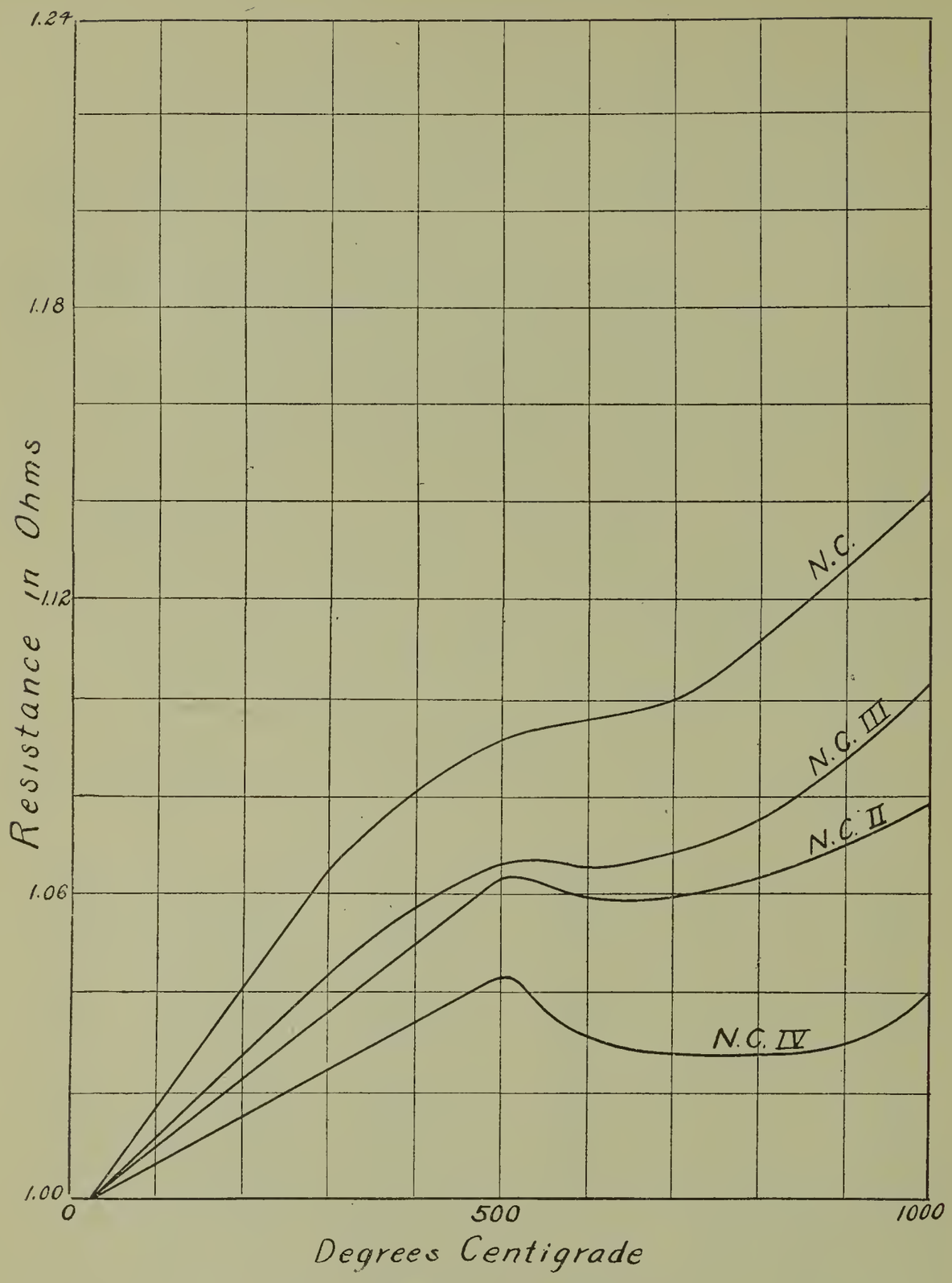


Fig. 3. Nickel-Iron-Chromium Wires

temperature coefficient over this range. Above 700° C. the curve rises sharply again.

In the Nichrome IV series the same general trend is followed, except that between 500° C. and 700° C. the wire has a marked negative temperature coefficient. This can be readily seen in Fig. 3 on which the results in Table IV are graphically plotted.

The temperature coefficients between 20 and 1,000° C. of alloys containing from 14 to 16 percent of chromium are not very different from one another, a fact which will be seen by comparing the values of the resistances of these alloys at 1,000° C. The temperature coefficients of the Nichrome IV series with chromium content above 17 percent appear, however, to drop sharply with increasing content of chromium.

In the figures for the resistivities of the alloys in the Nichrome III series, there appears at first sight to be a discrepancy in the relation between the resistivity and the content of chromium. This is to be explained by the fact that the wires measured had been subjected to varying degrees of oxidation. The normal resistivity of a bright annealed wire, containing 15 percent of chromium, is from 520 to 540 ohms per mil foot. When exposed to air and heated, the wire takes on an oxidized coat, and the apparent specific resistance of the material will rise to a degree corresponding to the thickness of the oxidized layer. These values then for the specific resistance of Nichrome III are the apparent, and not the true resistivities of the metal contained in the oxidized wire. This question of the change in the apparent resistivity of a bright wire on oxidation will be taken up at a later time.

Group B 2. Nickel-Iron-Chromium Wires.

The most important material in this group is the alloy which is manufactured under the trade name of Nichrome. It contains approximately 60 percent of nickel, 26 percent of iron and 12 percent of chromium. Its specific resistance is approximately 660 ohms per mil foot. This alloy is more extensively used than any other material for heating units running at high temperatures. It is a very satisfactory alloy for temperatures up to 900° C. It may be used for temperatures up to 1000° C., but at this latter temperature the oxidation of the material is rapid and the life of the unit is correspondingly short.

The variation in resistance of six different samples of Nichrome together with the analyses of the samples are given in Tables V and VI.

The class of alloys represented by Nichrome II are somewhat superior to Nichrome in their resistance to oxidation. The com-

position of the alloy is changed by increasing the amount of nickel and chromium in the alloy and reducing the content of iron. The specific resistance of the alloy is only slightly increased thereby.

One set of observations is given on an alloy containing over 30 percent chromium with nickel and iron, which was melted by Mr. W. T. Fuller of The General Electric Company. The material was excessively hard to draw to wire. It is doubtful whether this material represents a commercially practicable alloy.

With regard to the temperature coefficients of these alloys it will be seen from Fig. 3 that these alloys show the same change in slope at 500° C. In the case of the latter alloys containing 20 percent or more of chromium the temperature coefficient is negative for a short range of temperature above 500° C.

Group B 3. Iron-Chronium Wires.

The iron-chromium alloys have up to the present been used to only a slight extent in the heating industry. Some materials of this class are, however, to be found on the market today, so that some mention should be made of them.

The alloys are composed of approximately 75 percent iron and

TABLE V.

Variation in Resistance of Nickel-Iron-Chromium Wires.

NICHROME

Temp. °C	No. 2	No. 3	No. 8	No. 12	No. 9	No. 7
20	1.000	1.000	1.000	1.000	1.000	1.000
300	1.091	1.086	1.092	1.071	1.073	1.065
400	1.113	1.104	1.110	1.089	1.090	1.081
500	1.126	1.120	1.125	1.102	1.105	1.092
600	1.132	1.125	1.129	1.106	1.108	1.096
700	1.142	1.133	1.134	1.111	1.115	1.100
800	1.152	1.141	1.141	1.118	1.124	1.115
900	1.165	1.154	1.154	1.130	1.136	1.127
1000	1.182	1.172	1.171	1.148	1.150	1.142
Percent chromium..	10.75	10.90	11.05	11.45	11.70	12.05
Resist. at ohms/mil foot at room temp..	633	640	689	665	654	663

TABLE V.—*Continued.*

NICHROME II.

Temp. °C.	1	2	30 Percent Chromium
20	1.000	1.000	1.000
300	1.037	1.038	1.048
400	1.050	1.050	1.061
500	1.063	1.062	1.075
600	1.059	1.058	1.076
700	1.059	1.057	1.079
800	1.063	1.059	1.084
900	1.069	1.065	1.090
1000	1.078	1.072	1.098
Percent chromium	19.5	17.95	31.35
Resistance, ohms/mil foot at room temperature	668	683	686

TABLE VI.

Analyses of Nickel-Iron-Chromium Wires.

NICHROME.

No.	Ni	Fe	Cr	Mn
2	59.29	28.70	10.75	1.54
3	59.02	27.86	10.90	1.54
8	59.57	26.97	11.05	1.69
12	61.75	24.97	11.45	1.19
9	62.00	24.35	11.70	1.46
7	61.20	24.88	12.05	1.44
NICHROME II.				
1	....	....	19.5	....
2	69.35	10.53	17.95	1.58
30 PERCENT CHROMIUM.				
1	53.58	13.77	31.35	0

22 percent chromium, the high content of chromium being necessary to overcome the tendency of the iron contained in them, to oxidize. The silicon content of these materials sometimes runs as high as 2 percent so that this must be considered as an intentional addition.

From the manufacturer's standpoint the material is very hard

to draw, especially if it contains a relatively high silicon content. The specific resistance of alloys of this class is lower than the corresponding nickel alloys. Since, however, the temperature coefficient of the material is higher, the actual value of the specific resistance at high temperature is not materially different from the nickel-chromium alloys.

TABLE VII.

Variation in Resistance of Iron-Chromium Wires.

Temp. °C.	No. 1	No. 2
20	1.000	1.000
300	1.129	1.132
400	1.175	1.174
500	1.225	1.235
600	1.278	1.283
700	1.316	1.322
800	1.338	1.341
900	1.357	1.355
1000	1.375	1.365
Resistance, ohms/mil foot, at room temperature	583	....

Analyses of Iron-Chromium Wires.

No.	Fe	Cr	Ni	Si	C
1	75.10	22.06	0.87	1.67	0.18
2	74.62	22.23	1.17	1.24	0.65

These alloys withstand oxidation fairly well. They are, however, much inferior to nickel alloys containing 15 percent (Nichrome III) or 20 percent (Nichrome IV) of chromium. Another radical objection observed was that the wire under continued heating tended to grow materially in length.

The variation in the resistance of two of these alloys, and the specific resistance of one of them, are given in Table VII.

RELATIVE LIFE OF HIGH RESISTANCE WIRES.

The relative life of a number of these high resistance wires containing chromium with nickel or iron or both, has been investigated.

The wires were maintained at approximately 1000° C. for extended periods of time, in an electrically heated porcelain tube. The resistance of the wires was measured at known intervals of time, an increase in resistance denoting an oxidation of the wire. This test does not reproduce the conditions in a heating unit, since no current is flowing in the wire. It does, however, give a measure of the rate of oxidation of the various materials when exposed to air at a temperature of 1000° C.

TABLE VIII.

Increase in Resistance at 1,000° C.

Time Hours	Nickel-Chromium			Nickel-Iron-Chromium N. C. II	Maximum Temp. °C
	Percent Chronium			Percent Chromium	
	18.27	17.47	15.50	19.50	
0	1.000	1.000	1.000	1.000	1000
12	0.998	.996	0.996	1.008	1020
36	1.000	1.000	1.030	1.018	1030
61	1.006	1.029	1.085	1.028	1035
84	1.000	1.035	1.132	1.150	1046
114	1.000	1.057	1.143	1.171	1015
133	1.052	1.084	1.147	1.184	1033
161	1.058	1.093	1.163	1.197	1010
180	1.060	1.095	1.165	1.202	1030
206	1.061	1.098	1.168	1.205	1020
233	1.069	1.110	1.180	1.219	1033
260	1.073	1.118	1.188	1.228	1061
288	1.073	1.124	1.198	1.233	1016
306	1.075	1.126	1.202	1.238	1022
331	1.081	1.140	1.220	1.252	1053
357	1.087	1.176	1.258	1.318	1097
373	1.090	1.200	1.294	1.350	1083
430	1.094	1.243	1.363	1.382	1036
454	1.096	1.257	1.396	1.397	1095

In the first experiment various nickel-chromium wires were compared with one another and with a nickel-iron-chromium wire (N C II). The figures in the last column of Table VIII, under maximum temperature, represent the actual temperature of the furnace at the time when measurements were taken. The resistances observed at this temperature were then reduced to the values for 1000° C., which are those given in the respective columns.

At the conclusion of the experiment all of the materials were found to be very brittle indeed. The 18 percent material showed some unoxidized material still remaining in the core of the wire. The other wires were oxidized practically throughout.

The experiment shows conclusively that the life of a nickel-chromium wire bears a direct relation to the amount of chromium in the wire. For temperature in excess of 1,000° C. the chromium content should therefore be as high as possible. It has been al-

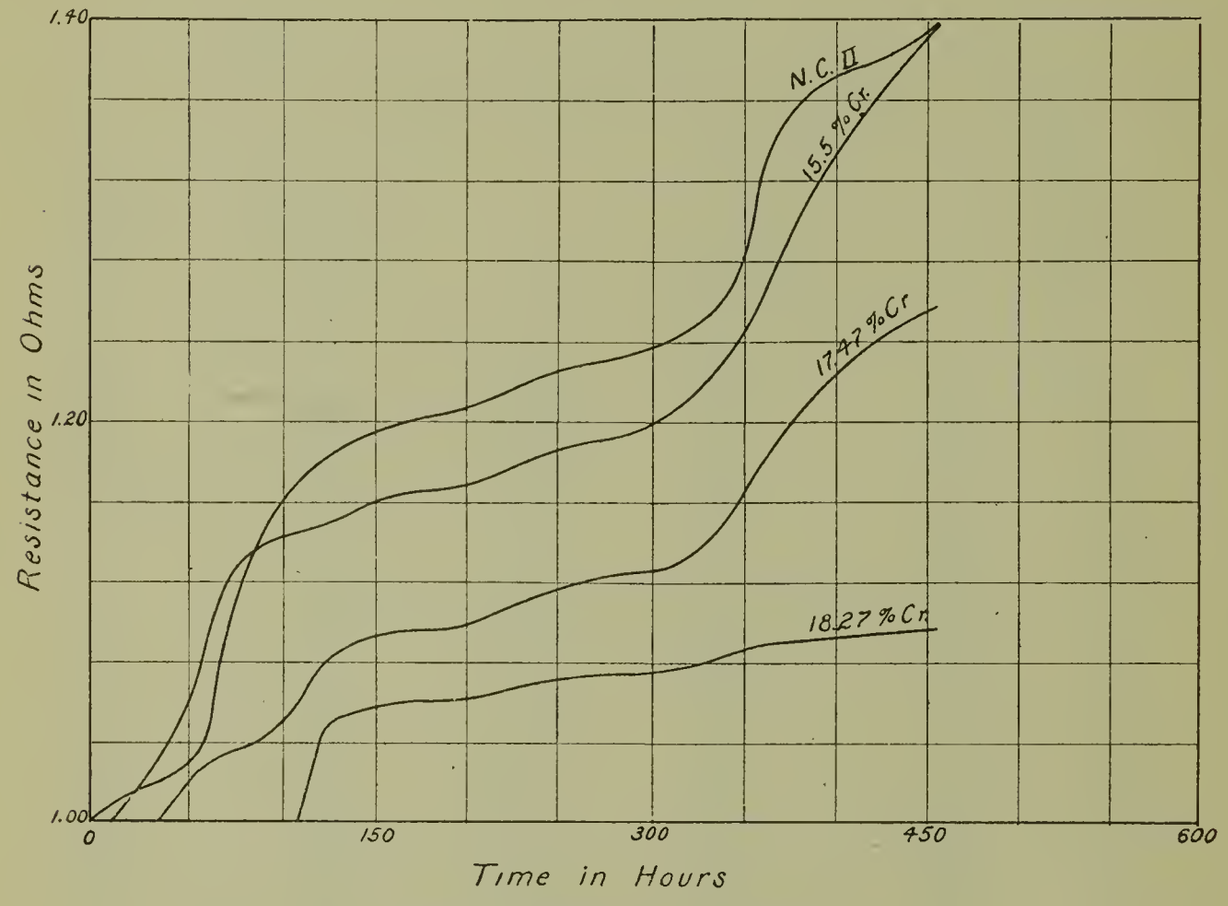


Fig. 4. Nickel-Chromium alloys

ready stated that alloys containing more than 20 percent of chromium are extremely difficult to draw to wire in the ordinary way. We may therefore consider this 20 percent alloy as having the most desirable manufacturing and operating characteristics.

Another experiment of a similar character was conducted to obtain a comparison between nickel-chromium and iron-chromium wires. See Table IX.

Two alloys of nickel-chromium containing approximately 17 and 15 percent chromium were tried out with an iron-chromium alloy containing 22.5 percent chromium. The furnace was main-

tained at approximately 1,000° C. for 160 hours, and at over 1,100° C. for 40 hours. At the end of that period all of the wires were practically destroyed. The iron-chromium wire shows a sharp increase in resistance at the end of 90 hours and thereafter increases slowly. This probably represents its useful life at this temperature. At the end of 160 hours the nickel-chromium wires had increased in resistance only 20 percent. At temperatures in excess of 1,100° C. the nickel-chromium wire containing

TABLE IX.

Comparative Life of Nickel-Chromium and Iron-Chromium Wires.

Hours	N.-C. IV	N.-C. III	FeCr	Max. Temp.
0	1.000	1.000	1.000	1000
11	1.000	1.000	1.042	951
18	1.005	1.015	1.055	1000
42	1.156	1.077	1.103	1050
66	1.151	1.080	1.204	973
90	1.162	1.100	2.301	1071
113	1.173	1.118	2.364	1038
138	1.174	1.129	2.402	1022
160	1.200	1.193	2.561	1076
166	1.259	1.365	2.744	1158
180	1.311	1.745	2.912	1146
185	1.320	1.831	2.933	1145
203	1.454	....	2.982	1144

the lower percentage of chromium increases much more rapidly in resistance than the wire containing the higher percentage of chromium—a fact which indicates that it is being more rapidly oxidized at this temperature.

BRIGHT WIRE.

The observations on the resistances of the various nickel-chromium wires indicated in the preceding paragraphs were all made on materials which had been superficially oxidized by exposure to air. In some cases the wires were measured while still retaining the oxide coat from the annealing process. In the case of a bright wire free from oxide, the material was first carried

to 1,000° C. in order to oxidize the surface and thereby stabilize its resistance.

There is, however, at the present time a tendency among the manufacturers to produce only bright wire, free from any trace of oxide on the surface. The reasons for this are more esthetic than utilitarian. The bright wire is especially desired by those users producing units in which the wire is exposed to the eye of the purchaser. It is seldom demanded by those who are producing any form of armored unit in which the wire is enclosed.

TABLE X.

Change in Resistance on Oxidation.

Material	Percent Chromium	Initial Resistance	End of First Heat	End of Second Heat	End of Third Heat
N C IV....	18.2	1.000	1.0433	1.0445	1.0452
N C IV....	17.5	1.000	1.0380	1.0405	1.0410
N C III....	15.5	1.000	1.0327	1.0343	1.0346
N C.....	12.7	1.000	1.0316	1.0312	1.0331

In this latter case the only advantage in having bright wire comes from the ease with which the electrical connections can be made. If oxidized wire is used the contact must be cleaned before the connection can be made.

Apart from the reasons given there would seem to be no advantage in using bright wire, because after the first hour of operation the unit made from bright wire will be in the same condition as a unit made from oxidized wire.

The first users of bright wire naturally complained that the constants which they had formerly used to determine the resistance of the older oxidized wire at any temperature no longer applied to the bright wire. It seemed advisable then to determine the relation which exists between the resistance of the initially bright wire and the same material after oxidation. Accordingly, coils of the various materials in the bright condition were oxidized by carrying them up to 1,000° C. in an electrically heated tube,

after which they were cooled to room temperature. The results are shown in Table X. The resistance of all materials are given at 20° C.

The results indicate that the resistance of a bright wire will increase on oxidation from 3 to 4.5 percent, according to the nature of the material. Since the wires were all initially in an annealed condition, this result is entirely due to the reduction in the effective diameter of the wire by oxidation. The protective action of the oxide coat is indicated by the fact that the later heats did not change the resistance of the wire by more than three parts in a thousand.

With this information the user of bright wire can easily find the resistance of the corresponding oxidized wire, and can then use the temperature coefficients given in the preceding tables for determining the resistance of the material at any temperature.

SUMMARY.

The materials used in the heating elements of commercial units may be divided into two classes. The first class comprises those which require materials with high specific resistance at the operating temperature. The second class includes those materials which in addition to having a high specific resistance must also withstand oxidation. The first class of materials can be operated successfully at temperatures not exceeding 500° C. The second class may be used with more or less satisfaction up to 1,100° C.

It will be possible from the data contained in this paper to calculate the specific resistance of any material in either class at any operating temperature.

In the first class the various grades of nickel have been investigated, together with two alloys of copper and nickel—Monel and Advance—and two alloys of iron and nickel—alloy No. 141 and alloy No. 193. In the second class the various grades of nichrome have been considered.

Some information on the relation between the resistances of bright and oxidized wire is also included in the report.

We desire in conclusion to express our appreciation to the mem-

bers of the technical staff of the Driver Harris Co. for their co-operation during the progress of this work.

Troy, N. Y.

DISCUSSION.

COLIN G. FINK[1]: It is so, is it not, that the higher the chromium percentage the more resistant to oxidation do the alloys become at elevated temperatures? Say you had an alloy of 60 percent chromium and 40 percent iron, would not that withstand oxidation at the elevated temperature of, say, 1,000° or 1,200° C., without deterioration, over a much longer time? Is it not merely a case of not knowing how to work these high chromium alloys down to fine wires that we have stopped at the low percentages mentioned by you?

M. A. HUNTER: Yes, I think Dr. Fink hit the nail on the head when he said, "if we had a high chromium wire." The whole point is that it can not be drawn.

COLIN G. FINK: That "can not" means we do not know how?

M. A. HUNTER: Yes, exactly. We have no dies at the present time which will stand up under the drawing effect of an alloy which is in excess of about 25 percent of chromium.

W. G. HARVEY[2]: The authors have brought out the different characteristics as far as ohmage is concerned. How do these different compositions and wires vary in their brittleness at high temperatures?

M. A. HUNTER: The user of the wire can tell you a lot more about the brittleness of the material during operation than I can, because I have only run laboratory tests on short samples of wires, and have usually carried out the tests in an accelerated way by pushing to extreme temperatures. But there is no doubt that when these wires are operated, eventually recrystallization occurs in the wires and they do become brittle. But at a tem-

[1] Consulting Electrometallurgist, New York City.
[2] Vice Pres. and Supt., American Magnesium Corp., Niagara Falls, N. Y.

perature of 1,100° C., running for 200 hours in an electrically heated tube, the 20 percent chromium wire had more residual flexibility left in it than the 15 percent chromium. That meant, not that there was a difference in the amount of crystallization in the two wires, but that the oxidation had proceeded deeper in the alloy which contained 15 percent than it had in the alloy containing 20 percent. I think that in the small ranges of composition that you have here—15 and 20 percent—there would not be any great difference in the amount of recrystallization and consequently in brittleness in the wire. None of the wires, however, will run in free air at 1,000° C. for more than 200 or 250 hours. Their life is exceedingly short.

COLIN G. FINK: Is it not usually a case of breaking down at the point of contact with the support, rather than recrystallization? For some wires asbestos as a support is not suitable, and the reaction taking place between the heated wire and the asbestos will cause a breakdown at that point long before recrystallization takes place in the rest of the wire.

M. A. HUNTER: Do you mean the connection between the wire itself, the heating element, and the lead-in wires?

COLIN G. FINK: No, I have reference, for example, to the winding of resistor wire over a thin strip of mica, or of placing the resistor wire over a sheet of asbestos. Heating the wire at 1,000° or 1,200° C. in contact with a silicate will cause a reaction to take place between the wire and the silicate.

M. A. HUNTER: There is one point I would like to mention here. Any silicate in contact with a chromium wire will cause a rapid deterioration, due chiefly to the formation of chromium silicates at that particular point. But the main reason for failure in resistance wires is not due to this cause, which I would call faulty design. Even if design of the unit is perfect, the wire still breaks down, usually from segregations in the material.

The ingots are made in 2,000 or 3,000-pound lots. No ingot is free from some kind of segregation. It may be carbides or silicides, or whatever the small residual impurities may be that are in the wire from the electric furnace operation. When you draw a wire to 20 mil, or 10 mil, if these segregations accumulate

at a particular spot they produce a hot spot in the wire and the wire will eventually break at that point. Failures are usually due to accumulation of segregations at a particular point, rather than to oxidation on the surface of the wire. If the wire is operated under forced conditions we find that to be particularly so. The wire will break down at a particular point, yet the rest of the wire will remain good.

F. S. WEISER[3]: What is the critical temperature at which this nichrome wire and silicate might react?

M. A. HUNTER: I have no information on that point. They certainly do react at 800° and 900° C., but what the minimum temperature is, I can not say.

E. F. COLLINS[4]: I have had a good deal of experience with these alloys in practical operation. I have had experience using both round and flat ribbon, and if you will read my paper you will notice I advocate use of the ribbon. I have found that the wire will not operate for the same life at the same temperature that a ribbon will. A part of the difference may lie in the manufacture of the material, a part of it comes from other sources. Therefore, while the temperatures named are much below that which we are running successfully on ribbon furnaces today, I will not dispute at all that it is too low if you are going to use wire for your resistors.

[3] Waterbury, Conn.
[4] Engineer, General Electric Co., Schenectady, N. Y.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 21, 1922, President Schlueder-berg in the Chair.

RESISTIVITIES OF SOME GRANULAR RESISTOR CARBONS.[1]

By Clyde E. Williams[2] and Gordon R. Shuck[3]

INTRODUCTION.

During the course of some experimental work being conducted at the Northwest Experiment Station of the U. S. Bureau of Mines in co-operation with the University of Washington, at Seattle, Washington, it became necessary to determine the electrical resistivities of a number of granular carbon resistor materials. Some of the results obtained are presented here with the hope that they may be of value in the work of others.

Granular resistor materials are used in the heating elements of some types of electric furnaces. The important requirements of a satisfactory resistor material are:

1. Small change in resistivity with different temperatures in order to avoid too much regulation of current.
2. A low ash content to obviate too frequent renewing of heating element.
3. High resistance to oxidation.
4. Sufficient density, physical strength, and hardness to withstand mechanical forces tending to break up particles.

Two common resistors are "granular resistor carbon" and "granular resistor graphite", both made from petroleum coke. Their contact resistivities have been measured, under certain conditions, and the values may be obtained from the manufacturers. Some results are found in the literature, but they are scattered and incomplete. The National Carbon Co.[4] gives the resistance of resistor carbon passing 0.25 in., remaining on 0.125 in. screen, under a pressure of 620 grams per sq. in. as 0.810 ohm per inch

[1] Manuscript received August 14, 1922. Published by permission of the Director of U. S Bureau of Mines.

[2] Metallurgist, U. S. Bureau of Mines, Seattle, Wash.
[3] Professor of Electrical Engineering, University of Washington, Seattle, Wash.

[4] National Carbon Co., Inc., The Carbon Electrode, New York, 1922.

cube at normal temperature, and 0.230 ohm per inch cube at 1000° C., and without pressure as 1.800 ohms per inch cube at room temperature and 0.600 ohm per inch cube at 1000° C. FitzGerald[5] discusses some of the theoretical aspects of resistivity and points out that when carbon is raised to a higher temperature than it has reached before, its resistivity is decreased and its density and resistance to oxidation are increased. From FitzGerald's data, Stansfield[6] by calculation obtained the values for granular graphitized coke given in Table I.

TABLE I.

Resistivity of Granular Graphitized Coke.

Material	Size of Grains.	Ohms per cu. inch		
		Cold	Red Hot	Red Hot Weighted
Graphite....	Through 5, on 6 mesh (Through 0.155, on 0.13 in.)	0.36	0.24	0.15
Graphite....	Through 3, on 4 mesh (Through 0.263, on 0.185 in.)	0.29	0.19	0.11

Jeffries[7] measured the resistivities of granular graphite, granular carbon, and Kryptol ("a mixture of carbon and some dilutent which is probably not a good conductor of electricity") packed in a small electric resistance furnace. The values shown in Table II at 20° C. and 1000° C. are taken from his curves.

Tucker, Doty, and Canchois[8] measured the resistivities of cokes at various temperatures up to about 500° C. and under various conditions. They found that cokes containing volatile matter had exceptionally high resistivities, which decreased when the coke was heated and the volatile matter driven off.

[5] F. A. J. FitzGerald, Materials for Resistors: Electrochemical Industry, 1904, 2, 490. Also Künstlicher Graphit: Monographien über angewandte Elektrochemie XV. Band, 1904.

[6] Alfred Stansfield, The Electric Furnace: 2d ed., McGraw-Hill Book Co., Inc., New York. (London: Hill Publishing Co., Ltd.) 1914

[7] Zay Jeffries, Notes on the Gran-Annular Electrical Furnace: Met. and Chem. Eng., 1914, **12**, 154.

[8] S. A. Tucker, A. Doty and R. W. Canchois, Granular Carbon Resistors: Trans. Am. Electrochem. Soc., 1907, **12**, 171.

DESCRIPTION OF FURNACE AND OPERATIONS.

In the work described in this paper, contact resistivities of materials made from various cokes, charcoals, resistor carbon, and resistor graphite were determined under conditions similar to those met with in commercial furnaces. The shape of the resistor compartment in a furnace might materially change the total resistivity of the heating element. A deep narrow channel will have less resistance than a shallow wide one of the same cross-sectional area. If it is assumed that the resistor material is divided into several horizontal strata, the lower layers will be under pressure due to the weight of the layers above, and consequently will have less resistance and greater current density than the layer above. Hence the I^2R heat generation will be greatest

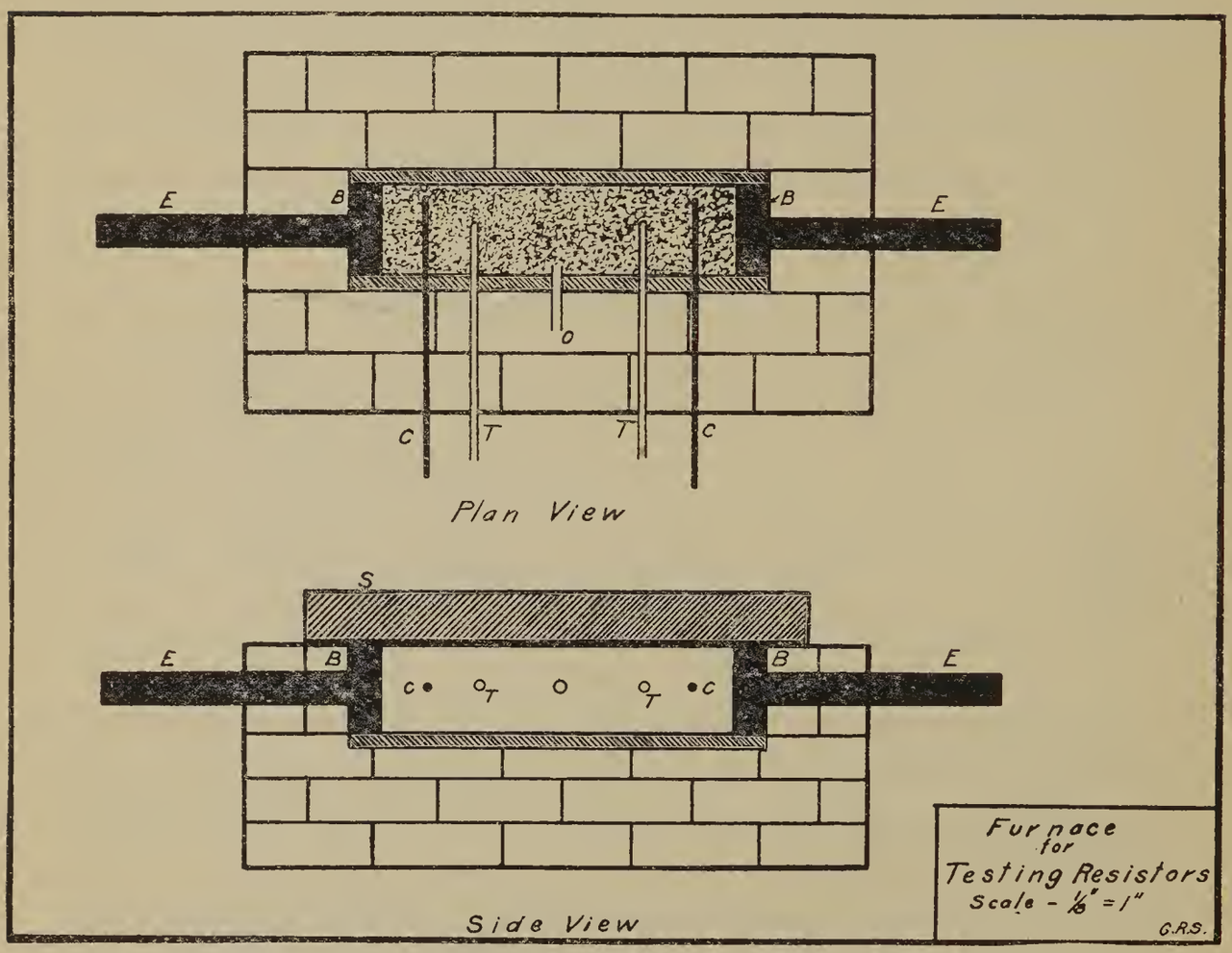
TABLE II.

Material	Screen Size	Resistivity Ohms per cu. in.	
		20° C.	1000° C.
Graphite	Through 0.093 in., on 0.033 in.	1.75	0.65
Carbon	Through 0.093 in., on 0.033 in.	4.80	0.70
Kryptol	Through 0.093 in., on 0.033 in.	8.30	1.90

in the lower portion of the resistor, which as a result will become hotter than the upper portion. This uneven heat distribution will be aggravated as the resistor becomes hotter, due to the negative temperature coefficient of resistors of this nature, and will be modified by the conduction and convection of heat upward. The inside lining of the resistor compartment may be a conductor of electricity, especially at the higher temperatures, and thus affect the conductivity of the resistor as a whole.

The furnace used in these tests was designed to give as uniform a temperature throughout the mass of resistor material as possible. The resistor compartment was 6 inches square and 24 inches long (15.2 x 15.2 x 61 cm.) the sides and bottom were 9 inches (23 cm.) thick, made of silica brick, and lined with a 0.5 in. (13 mm.) layer of alundum cement. Each end consisted of a block of carbon, B, 6 inches square and 2 inches thick, (15.2 x

15.2 x 5 cm.) in the center of which a 2-in. (5 cm.) round graphite electrode, E, was imbedded in carbon paste, and extended out through the silica brick end-walls to the electrical leads. The top of the furnace was covered by a slab of fire clay, S, which rested on the side walls of the furnace and was cemented into place after the compartment was filled with resistor material. 0.375-in. (9.5 mm.) carbon rods, C, placed horizontally 18 in. (46 cm.) apart, extended through one side of the furnace into the resistor material



nearly to the opposite wall. These rods were connected to the leads of a voltmeter. Three inches (7.6 cm.) from and parallel with each of the carbon rods a refractory tube, T, 0.25 in. (6.4 mm.) inside diameter, extended through the wall into the center of the charge, and served as thermocouple receptacles Both alundum and fused quartz tubes were used, the alundum proving more satisfactory. The lower temperatures were taken with copper-constantan, and the higher ones with platinum-platinum rhodium thermocouples. For measuring temperatures above 1200° C. an alundum tube 0.5-

inch (13 mm.) in diameter and sealed at one end was inserted at O and the hot resistor material viewed with an optical pyrometer.

Low voltage alternating current power was used for heating the charge and for determining the resistance. The power input was controlled by means of an induction regulator capable of giving a variation of voltage from 0 to 480 volts. No attempt was made to keep the voltage or current constant. The power input was varied so as to obtain a uniform rise in temperature from room to 1200° C. in three hours.

The resistor materials were prepared by heating for several hours at a temperature of about 1000° C. to drive out volatile matter, crushing, and sizing. The resistor compartment was then filled with the material to be studied, the cover fitted into place so as not to rest on the resistor material, the charge heated to about 1200° C. and allowed to cool without being further disturbed. Then the power was again turned on and readings of temperature, amperes, and volts taken at short intervals. The temperature was run up to 1200° C. usually, although in some cases readings were taken up to 1600° C. In all cases, the resistivities were calculated to ohms per cu. in.

RESULTS OBTAINED.

Granular graphite. Granular resistor graphite passing 0.5, on 0.25 in. in size was first tested. The temperature was gradually raised to 1600° C. and then allowed to decrease, with the power still on, readings being taken until the mass had cooled to 1200° C. Curve 1, Fig. 1, shows the relation between resistivity and temperature. It will be noted that as the temperature rises above 1000° C. the resistivity increases. This phenomenon occurred when the other materials were tested, but was of greater magnitude with graphite, resistor carbon, and coal-tar coke, all low-ash materials, than with the high-ash cokes. After the mass began to cool from 1600° C., the resistivity decreased, the curve showing the change in resistivity with temperature starting back on a short cut toward the origin.

Granular carbon. Measurements were made of two different sizes of granular resistor carbon supplied by the National Carbon Co., the temperature being carried up to 1200° C. in both tests.

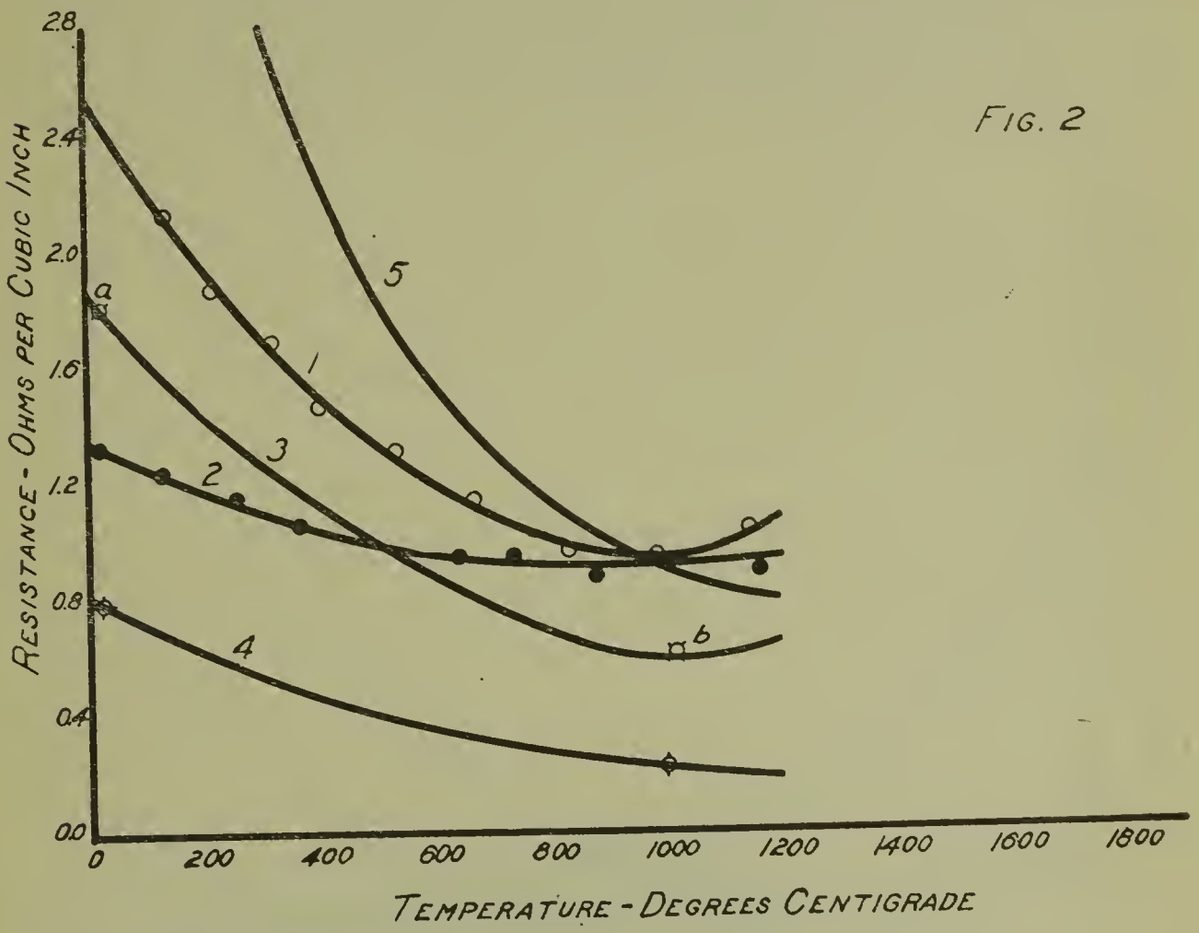
Curves 1 and 2, Fig. 2, show the changes in resistivity with changes in temperature for the sizes through 0.25-inch, on 0.125-inch and through 0.5-inch on 0.375-inch, respectively. Curve 3, Fig. 2, was plotted between points a and b, representing values given by the National Carbon Co.[9] for 0.25 on 0.125-inch granular resistor carbon and is lower than Curve 1, showing the divergence in results that may be obtained by different investigators. The relative changes in resistivity with the temperature are about

Granular graphite resistor material;
Screen size, through 0.5 in. on 0.125 in.

the same for the two curves, showing that although the actual resistivity values obtained by the different investigators are different, the thermal coefficients are the same. See Table III. Curve 4, Fig. 2, was plotted from values supplied by the National Carbon Co.[10] and shows the effect of pressure on the resistivity. The thermal coefficient is of the same magnitude as that obtained for material not under pressure. See Table III.

[9] National Carbon Co., Inc., The Carbon Electrode, New York, 1922.
[10] National Carbon Co., Inc., The Carbon Electrode, New York, 1922.

Curve 5 (from Jeffries,[11]), Fig. 2, is drawn for granular carbon particles 0.093-in. to 0.03 in. in size, and, with curves 1 and 2, shows that the resistivity increases as the size of the particles of carbon decreases. From Curves 1, 2, 3, and 5, it is seen that the difference in resistivities at the higher temperatures is very small.



Granular resistor carbon;

Curve 1. Screen size—through 0.25 in. on 0.125 in.
Curve 2. Screen size—through 0.5 in. on 0.375 in.
Curve 3. Screen size—through 0.25 in. on 0.125 in. Results taken from the National Carbon Co.'s "The Carbon Electrode."
Curve 4. Screen size—through 0.25 in. on 0.125 in. under pressure of 2.7 lb. per sq. in. Results taken from "The Carbon Electrode."
Curve 5. Screen size—through 0.03 in. on 0.09 in. Results taken from Jeffries, Chem. and Met., **12**, 155.

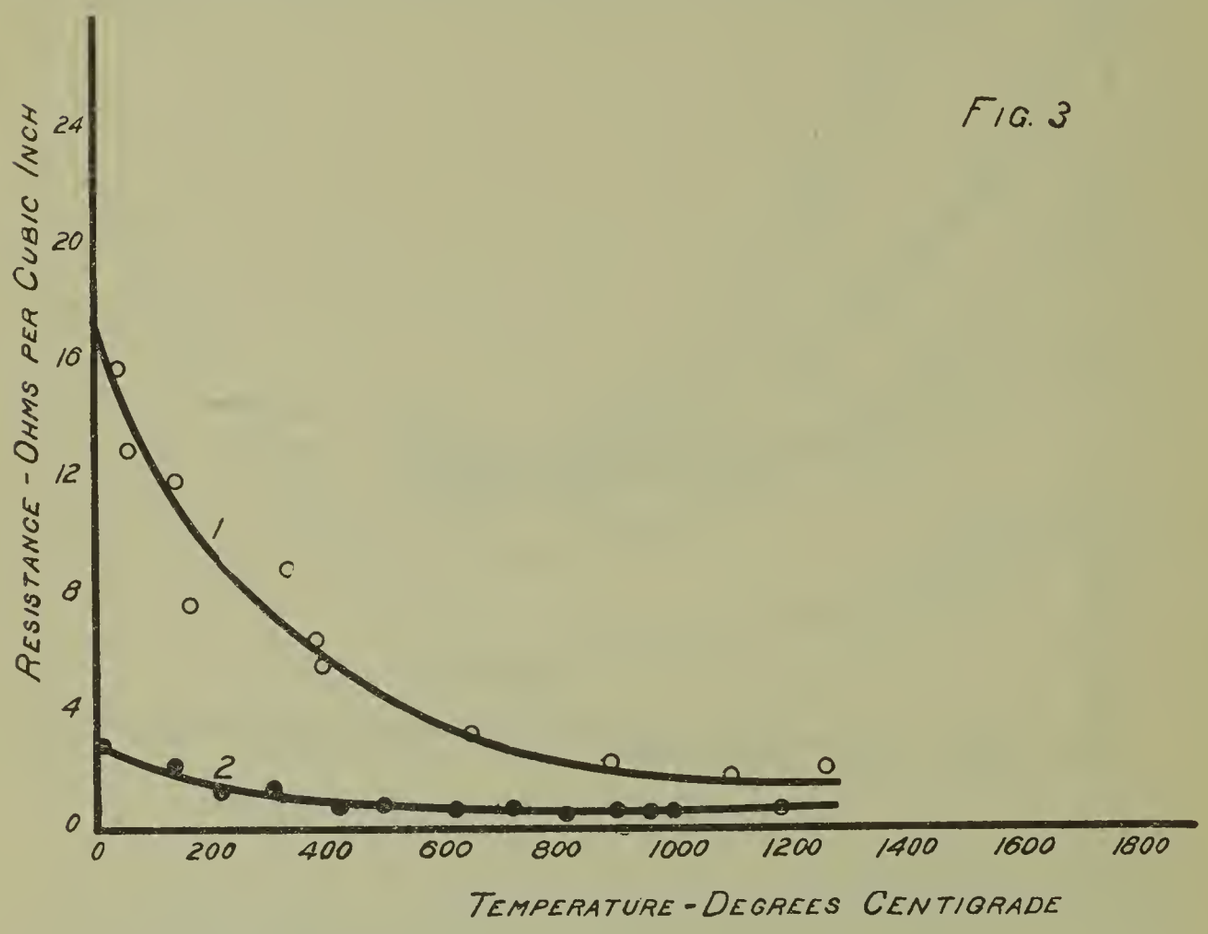
This relation holds for other materials and is true for all the types of carbon resistor materials tested.

Cokes and charcoal. A local gas-house coke containing 24 percent ash and 6 percent volatile matter was tested, Curve 1, Fig. 3, being obtained. Most of the volatile matter was driven out during this heating and the test was repeated, Curve 2 being obtained. Upon repeating this procedure three times, values were

[11] Zay Jeffries, Notes on the Gran-Annular Electrical Furnace: Met. and Chem. Eng. 1914, **12**, 154.

found which in each case fell either upon Curve 2 or very close to it, showing that under the conditions of the experiment, the values obtained in the second test are not changed by further heating. Similar results were obtained with another coke (from Utah) containing 13 percent ash.

With charcoal containing 14 percent volatile matter, no deflection of the ammeter needle could be obtained, even when 480 volts

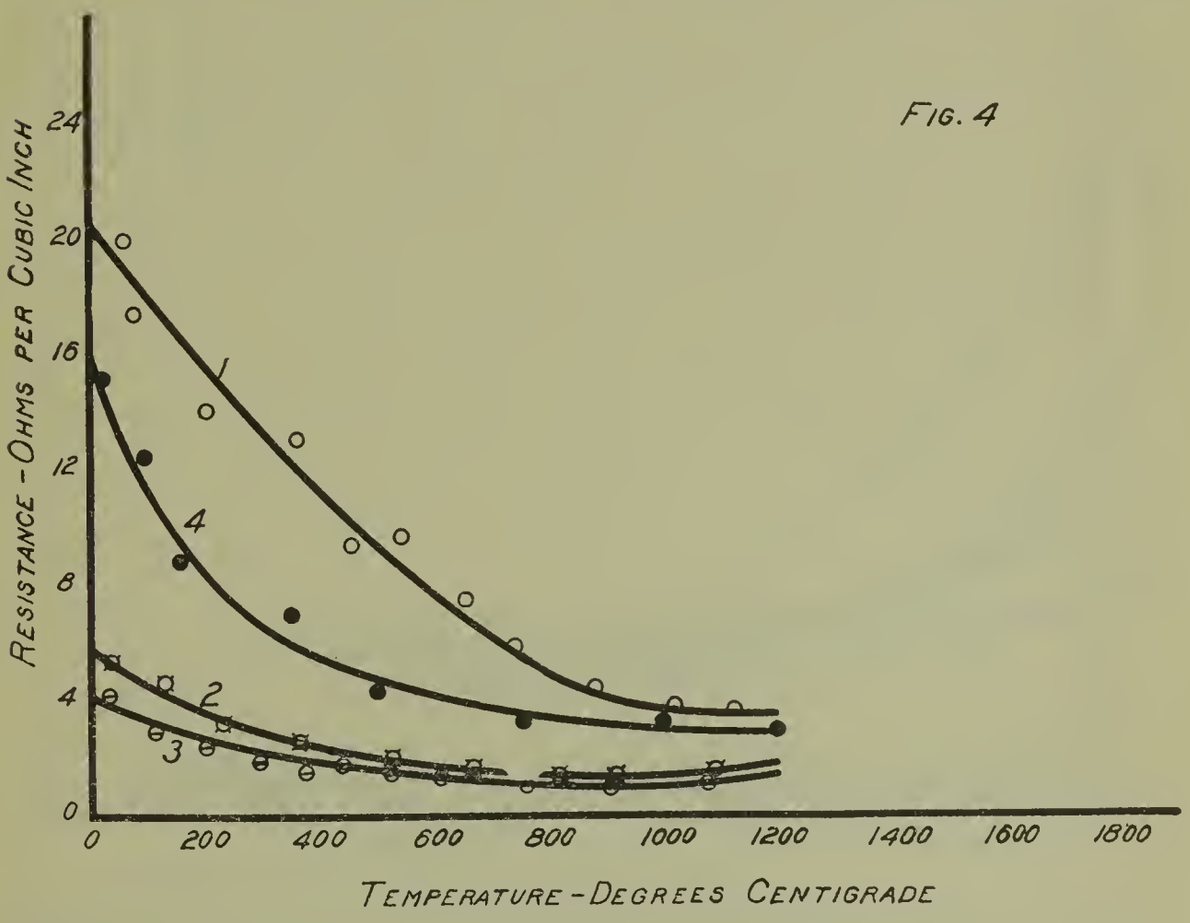


Gas-house coke (Washington).
Size of screen, through 0.5 in. on 0.25 in.
Curve 1. First heating. Contained volatile matter.
Curve 2. Third heating. Contained practically no volatile matter.

were impressed across the terminals. After part of the volatile matter had been removed by heating externally, Curves 1, 2, and 3, Fig. 4, representing successive heatings of the same charge, were obtained. Similarly, it was found that coal-tar residue containing 4 percent volatile matter would not conduct the current when 480 volts were impressed, but that after it had been heated and the volatile matter driven out it became an excellent conductor. The high resistivity during the first heating was undoubtedly due to the high volatile content of the resistor material.

Fig. 5 compares the curves for the various types of materials used. Curve 1 is for Acheson graphite, curve 2 for resistor carbon, curve 3 for retort carbon containing 2.0 percent ash, curve 4 for wood charcoal containing 2.0 percent ash, curve 5 for a product containing 30 percent ash obtained by carbonizing non-coking sub-bituminous coal from Issaquah, Washington, curve 6 for a local gas-house coke, containing 24 percent ash, made from coal from Carbonado, Wash., and curve 7 for coal-tar coke con-

FIG. 4



Wood charcoal (fir). Size of screen—through 0.5 in. on 0.25 in.
Curve 1. First heating, contained at beginning 10 percent volatile matter.
Curve 2. Second heating contained 1 percent volatile matter.
Curve 3. Third and fourth heatings contained less than one percent volatile matter.
Curve 4. Third heating of charcoal containing 20 percent siliceous material mixed with charge.

taining 0.5 percent ash. The graphite was sized to pass a 0.5-inch and to remain on a 0.125-inch screen, all the other products being sized to pass a 0.5-inch and to remain on a 0.25-inch screen.

These curves (Fig. 5) show that the various types of carbon may be divided according to their resistivities, into three main divisions, as follows:

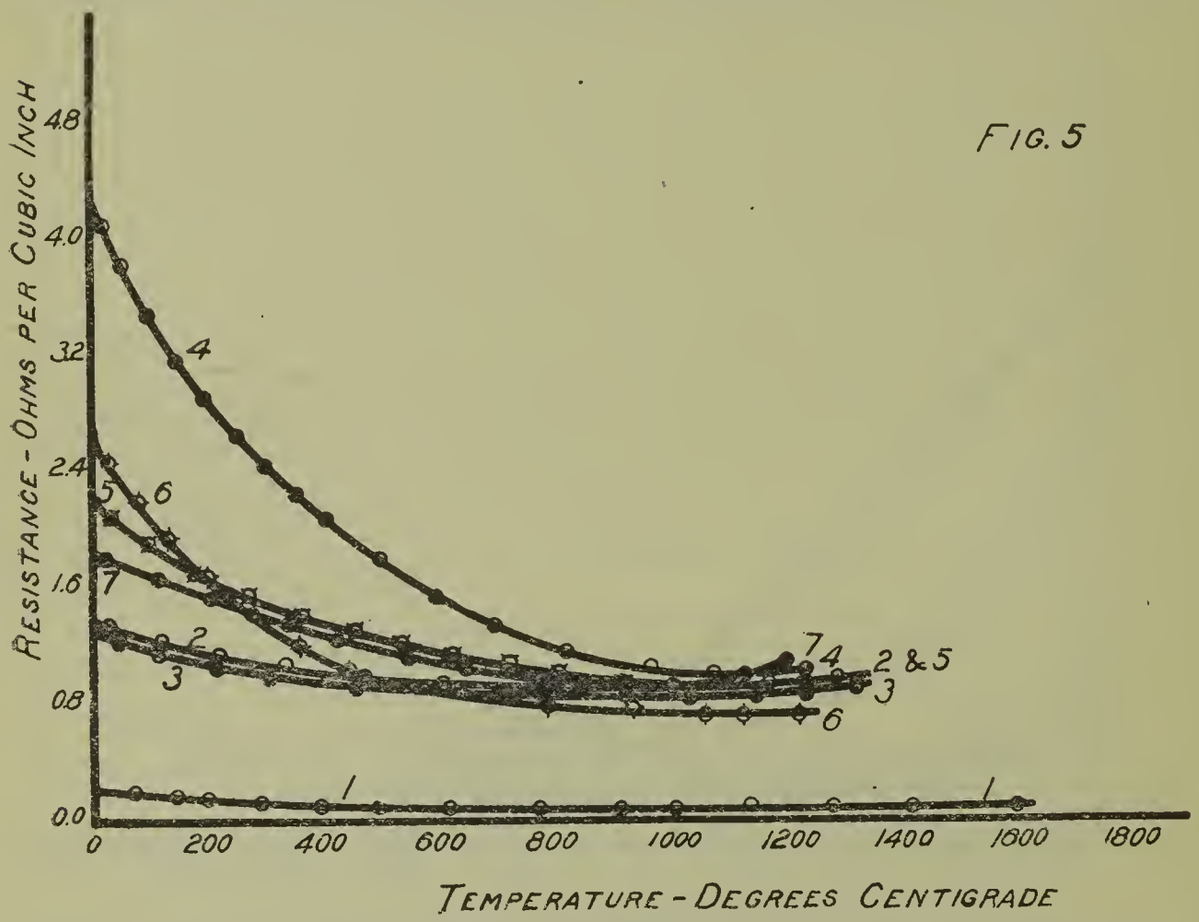
1. Graphitized carbon with low resistance;

2. Amorphous carbon, except wood charcoal, with medium resistance, and,

3. Wood charcoal with high resistance.

Class 2, amorphous carbons, should be subdivided into (1) those substances practically free from ash, as, for example, resistor carbon and retort carbon, and (2) those of high ash content and those containing a small amount of volatile matter, such as the ordinary cokes, charred coals, or coal-tar coke. Ash

FIG. 5



Curve 1. Granular resistor graphite through 0.5 in. on 0.125 in. Ash 0.25 percent.
Curve 2. Granular resistor carbon through 0.5 in. on 0.375 in. Ash 0.45 percent.
Curve 3. Retort carbon through 0.5 in. on 0.25 in. Ash 2.0 percent.
Curve 4. Charcoal through 0.5 in. on 0.25 in. Ash 2.5 percent.
Curve 5. Charred non-coking coal through 0.5 in. on 0.25 in. Ash 31.0 percent.
Curve 6. Gas-house coke through 0.5 in. on 0.25 in. Ash 24.0 percent.
Curve 7. Coal-tar coke through 0.5 in. on 0.25 in. Ash 0.50 percent.

content affects the conductivity, but not to the extent that is ordinarily supposed. The presence of a small quantity of volatile matter in the carbon increases the resistivity to a large degree. For example, the curve for coal-tar coke (7), which contained 0.5 percent ash and only 1 percent volatile, is much higher than Curve 3 for retort carbon, which contained 2.0 percent ash and 0.3 percent volatile matter, and yet it lies close to Curve 5 for charred non-coking coal containing 31 percent ash. The resis-

tivities obtained for Utah coke (see Table III), which contained 13 percent ash, were slightly higher for the same temperatures than those obtained for Washington coke, which contained 24 percent ash.

EFFECT OF IMPURITIES.

The effect of the presence of added impurities is shown in Fig. 4. Curve 3 is for charcoal and curve 4 for the same charcoal mixed with 20 percent siliceous material. It is seen from these curves that the presence of extraneous impurities increased the resistivity, whereas it was pointed out in discussing Fig. 5 that the high-ash content of some of the cokes did not increase the resistivity to a marked degree. It would appear, therefore, that as long as the impurity is contained within the conducting particle, the resistivity is not materially changed, because the greater part of the resistance is due to the contact between the particles of carbon and not to the resistance of the particle itself. High ash carbons used in commercial practice would be satisfactory until combustion of the contained carbon had continued to the point where ash was left in a free state. Then the resistivity would increase, fusing or sintering of the ash would take place if the temperature were high enough, and bridging of the resistor material would result.

In these tests, it was observed that repeated heating of the resistor material decreased its resistivity until a certain point was reached where further heating produced no noticeable change. This change in resistivity is due almost entirely to the reduction of volatile matter and when all the volatile matter has been driven out no further change is observed. Some of the decrease in resistivity may be due to the gradual graphitization of the carbon and some to the conversion of the mineral matter (largely silicates) contained in the charge into more conductive carbides, although these actions would be extremely slow and were of too small magnitude to affect the results in these tests to a measurable degree. Examination of the charges resulting from the final heatings revealed the presence of unchanged particles of the mineral matter originally present, indicating that not much change had taken place. Undoubtedly changes of greater magnitude would have taken place had the temperature been raised a few hundred degrees.

Table III shows the resistivities and temperature coefficients of resistivity of the various materials tested. The temperature coefficient, a, was calculated from the equation

$$R_t = R_1 \left[1 + a_1 (t - t_1) \right]$$

in which R_t is the resistance at temperature t or 1000° C., and R_1 is the resistance at temperature t_1 or 20° C.

TABLE III.

Resistivity of Various Materials.

Resistor Material	Size, Inches		Ash Content	Resistivity Ohms per cu. in.		Temperature Coefficient of Resistance
	Passing	on		20° C.	1000° C.	
1. Acheson graphite..	0.5	0.25	0.25	0.175	0.085	—0.00052
2. National carbon...	0.5	0.375	0.45	1.3	0.90	—0.00032
3. National carbon...	0.25	0.125	0.45	2.4	0.95	—0.00061
4. *National carbon...	0.25	0.125		1.8	0.6	—0.00068
5. *National carbon 600 gm. per sq. in. pressure	0.25	0.125		0.81	0.23	—0.00073
6. Retort carbon	0.5	0.25	2.0	1.27	0.83	—0.00036
7. Coal-tar residue ...	0.5	0.25	0.50	1.9	1.0	—0.00048
8. Carbonized non-coking coal (Tono)	0.5	0.25	26.0	2.8	1.5	—0.00047
9. Gashouse coke	0.5	0.25	24.0	2.55	0.65	—0.00075
10. Utah coke	0.5	0.25	14.0	3.7	1.5	—0.00061
11. Carbonized non-coking coal	0.5	0.25	31.0	2.1	1.0	—0.00053
12. Charcoal	0.5	0.25	2.5	4.0	1.1	—0.00073
13. Charcoal mixed 20 percent siliceous material	0.5	0.25	22.5	12.5	3.5	—0.00074

* Calculated from values taken from The Carbon Electrode.[12]

The coefficient of resistivity seems to bear no relation to the ash content or to the type of carbon except in the case of charcoal and in the case where foreign material was added (Nos. 12 and 13, Table III) in which cases the coefficient seems to be larger. A high volatile content causes a large coefficient of resistivity, but sufficient measurements have not been made to establish definitely the limits. By comparing 2 and 3 in Table III, it is seen that different sized particles of the same material have different

[12] National Carbon Co., Inc., The Carbon Electrode, New York, 1922.

coefficients, and that the variation in amount is as great as that between two entirely different types of carbon.

SUMMARY.

1. The resistivities of several different types of carbon have been measured. It is not suggested that these materials be used for resistors, their characteristics being described so that their limitations may be seen. The information should be of value for purposes other than the design and operation of resistance furnaces. For example, in the operation of electric smelting furnaces it is of value to know the electrical resistances of the various reducing agents that may be used, and in the operation of melting furnaces the resistivity of the carburizer should be known.

2. The difference in resistivities of various types and sizes of carbon resistors is not very large at 1000° C. to 1200° C.

3. The temperature coefficient of resistivity is negative for all the forms of carbon tested up to 1000 or 1200° C., at which temperature it approaches zero and then becomes positive as the temperature increases further. This change was more pronounced in graphite than in the other forms of carbon.

4. High resistivities are caused by the presence of volatile matter in the resistor material, the resistivity and volatile matter bearing a direct relation for the same material.

5. Ash contained within the particle of carbon increases the contact resistivity and the thermal coefficient somewhat, but the effect is not nearly so large as is that of contained volatile matter. Extraneous ash or foreign matter of high resistivity increases the resistivity and the thermal coefficient to a very marked extent.

DISCUSSION.

H. C. P. WEBER[1]: In connection with this paper, it seems to me that the whole question is one of the economical value of the process. From a statistical point of view the question of course is, what can you get, assuming, for instance, you want to run a furnace at 1200° C? To me the question seems, what is the variation to be expected with the ordinary thermal processes depending upon oxidation in one form or another? What is the variation to be expected under the same conditions

[1] Res. Engr., Westinghouse Elec. & Mfg. Co., E. Pittsburgh, Pa.

with electrical heating? Does not the advantage of electrical heating lie in the possibility of sharper control of conditions?

F. A. J. FITZGERALD[2]: According to Mr. Williams, the temperature co-efficient of resistivity is negative for all forms of carbon tested up to 1000° or 1200° C., at which temperature it approaches zero and then becomes positive as the temperature increases further. This is a characteristic phenomenon, but I think if the temperature was carried to higher points than those attained in Mr. Williams' experiment it would be found that the co-efficient again becomes negative.

In working the carborundum furnace or the graphitizing furnace, the resistance curve at first drops rapidly, then increases for a time, but again drops to a lower point than it reached before, finally becoming practically a horizontal line.

DWIGHT D. MILLER[3]: Regarding the carbon resistor furnace, I have had quite a little experience with the Bailey type furnace, which you all know is based entirely upon the carbon resistor element. There is a circular trough, eight inches deep and anywhere from eight to twelve inches wide. We shot current through a carbon or graphite block. After operating a week or ten days we noticed there would be a film about a sixteenth of an inch that had formed on top, due apparently to oxidation. There was a certain amount of ash formed there, which would cut down the conductivity of that particular portion. But in comparing a sixteenth of an inch to eight inches in depth, the relative value was so small that the resistance as a whole, and therefore the conductivity of the trough as a whole, was slightly affected. There appears to be a certain amount of graphitization of the carbon taking place, due to the intense heat. The decreased resistivity of the graphite offsets the increase in resistance caused by the formation of ash of the carbon, and the resistance of the trough as a whole, therefore, stays nearly constant. That is the principle upon which these furnaces have worked for the last five or six years.

The main feature of industrial electric heating is "control." You have absolute control of all the factors that enter into metallurgical operation, whether it is melting, heat treating, atmosphere, flow of current, or time.

[2] FitzGerald Labs., Niagara Falls, N. Y.
[3] Engineer, New York City.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 22, 1922, President Schlueder-berg in the Chair.

THE DEVELOPMENT OF INDUSTRIAL ELECTRIC HEATING FOR LOW TEMPERATURE ENAMELING.[1]

By Wirt S. Scott[2]

Abstract.

Early experiments are recorded which point out the great importance of adequate ventilation of an electric enameling oven. During the drying of the enamel, combustible gases are evolved, and these must be withdrawn in such a way as to avoid explosions. The suspension and arrangement of the heating units is discussed. Typical electric oven installations of the automotive and typewriter industries are illustrated and described in detail.

[C. G. F.]

The development of the electrically heated enameling oven within the past 7 years is due to a concentration of effort on the part of electrical manufacturers and central stations upon a single industry—the automotive; and was accelerated by a willingness on the part of that industry to co-operate.

Previous to this development, the ovens were heated with gas, the burners being usually placed directly in the oven, and the heating being accomplished by the heated air of combustion bathing the work *en route* to the ventilation ducts placed in the roof of the oven. The ovens were poorly constructed, practically no attention being paid to thermal insulation, due to the low price of fuel. The art of enameling was extremely crude, the enameling departments being at the mercy of men who professed to possess so-called "trade secrets", the majority of whom knew little about the technique of enameling, and were at a loss to account for the large percentage of rejects that frequently occurred.

[1] Manuscript received August 19, 1922.

[2] Manager, Industrial Heating Section, Westinghouse Electric and Mfg. Co., East Pittsburgh, Pa.

The first experiments made to electrify enameling ovens, consisted in placing makeshift electric heating units in old gas ovens. Practically nothing was known as to the chemical action resulting from the baking of enamels, hence the first effort was to duplicate the results then being obtained with gas. Enamels of the kind under consideration consist of an asphaltic compound, carried in a suitable solvent with enough oil to make it resilient after baking. It was known that the solvent was driven off, and that the oils underwent oxidation, but practically nothing was known as to the ventilation problem involved. In burning the gas directly within the oven, an excessive amount of air was necessarily and fortunately introduced, automatically and unintentionally taking care of a condition that was not generally known to exist.

The first experiments using electric heat disclosed three points of advantage, namely, elimination of fires due to a combustible fuel, reduction in time required for baking, and a baked product having a smoother surface. Tests subsequently made by the research department of the Detroit Edison Co. revealed the fact that the baking in an electrically heated oven was accomplished largely by radiant heat, which seemed to penetrate the enamel quicker and to a greater depth than when heated by convection currents as in the direct gas ovens. The lack of products of combustion within the oven accounted for a cleaner product.

It was found, however, that the cost of operation was excessive as compared to gas, and knowing that a large amount of heat was being carried off in the vent ducts, it was thought that this source of loss could be eliminated, since no air was required for combustion. The first experiment consisted in closing up the oven as tightly as possible, and attempting to bake, but it was discovered that the enamel would not bake, regardless of the length of time that work was in the oven, but remaining in a "tacky" condition. This brought out the fact that a certain amount of air was required for oxidizing the enamel.

A continuation of these tests to determine the proper amount of air for oxidizing purposes resulted in a violent explosion of the oven, which almost completely demolished it. This forcefully brought attention to the composition of the enamel, which was found to consist of approximately 50 percent naphtha as a solvent for the asphaltum. This naphtha was distilled off as a gas. Most

of the heating elements used then were operating at a temperature of approximately 900° F., (482° C.) hence it was thought that if heaters were designed to operate at sufficiently low temperature, the ignition of the naphtha vapors could be eliminated, and a restricted amount of ventilation be used.

A small test oven was constructed, electrically heated, with positive means for controlling the air entering, and the gases leaving the oven. Samples of many kinds of enamels were obtained and subjected to the same tests. These experiments consisted in placing a small vessel containing enamel within the oven, and with the inlet and discharge ducts closed, raising the temperature of the oven to a high temperature, cutting off the heaters to insure a stabilized uniform temperature within the oven, then opening the inlet and next the exhaust duct. Within a few seconds after opening the vent ducts, an explosion would occur. Similar experiments were made at reduced temperatures, with explosions in each case. Explosions were readily obtained at a temperature of 550° F., (288° C.) and in several cases, at the baking temperature of the enamel itself, demonstrating the impracticability of attempting to operate with a heating element of sufficiently low temperature to eliminate the possibility of explosions when restricting the ventilation.

During these tests, it was noted that after each explosion the flames appeared to burn from the floor. It was first thought that this was the result of the enamel being blown out of the container, but more thorough investigation disclosed that the flame was due to the ignition of the volatile gases, which appeared to settle on the floor. Tests were then made to determine definitely the action of the volatile gases within the oven, and it was found that they were heavier than air and would first descend to the floor, filling up the oven like so much water. The gases were driven off very rapidly upon heating, consequently, before the baking temperature was reached, the mixture within the oven would be too rich to explode. Upon releasing some of the gas and admitting fresh air, the proper explosive mixture would be obtained. Under normal conditions of ventilation, the gases, after descending to the floor, would become heated, and ascend to the roof, passing out through the vent duct.

As a result of these tests, the following facts were established:

1. With restricted ventilation, explosions were possible in enameling ovens, regardless of the temperature of the heating element.

2. A sufficient amount of air must be admitted to the oven to keep the mixture "lean", or sufficiently dilute to make an explosion impossible.

3. The vapors should be withdrawn at or as near the floor as possible.

The first oven to be put in operation using the floor method of ventilation was also equipped with the roof method of ventilation in case the former failed, or it was found necessary to use a combination of both. Air was admitted back of the heaters. Tests not only showed that it was possible to ventilate from the floor, but that it was the proper way of ventilating when volatile gases must be removed. Repeated tests showed that one-third less air could be used when ventilating from the floor, and that the length of time required for baking was reduced 25 percent.

The reduction in the time required for baking was not an unlooked for advantage. Heaters, as well as gas burners, were restricted as to location within the oven. The work, after being dipped or sprayed with enamel, is allowed to drip or "set" before entering the oven. Upon heating, the enamel softens, and a certain amount flows off, dripping on the floor. Heaters placed on the floor under the work would soon be covered with enamel, the coking of which would ultimately cause a fire, even if the enamel did not ignite immediately when coming in contact with the heating element. For this reason it was found advisable to place the heaters along the side wall, but as near the floor as possible. With heaters placed in this position, and ventilating at the roof, the direct path for the heated air was up the side walls, across the roof, and out. This left a large space in the middle of the oven difficult to heat, the work necessarily remaining in the oven until that space was heated. In order to heat the coldest portion of the oven up to the desired temperature, the other parts had to be considerably overheated, which was not evident since the thermometer bulb was placed in the door, the coldest part of the oven. Ventilating from the floor, the heated air passed up along the side walls across the roof, and down through the middle of

the oven, and out, producing a much more uniform distribution of temperature by bringing the hot air through the middle of the oven and down to the cold floor.

Simultaneous with these tests, oven builders were being interested in designing and building better insulated ovens, and it was soon demonstrated that an oven having 4 inches of high grade insulation was a paying investment over one having 1.5 inches of poor insulation, which was then standard practice.

Furthermore, attention was called to the enormous amount of through metal in the form of bolts and channel iron extending

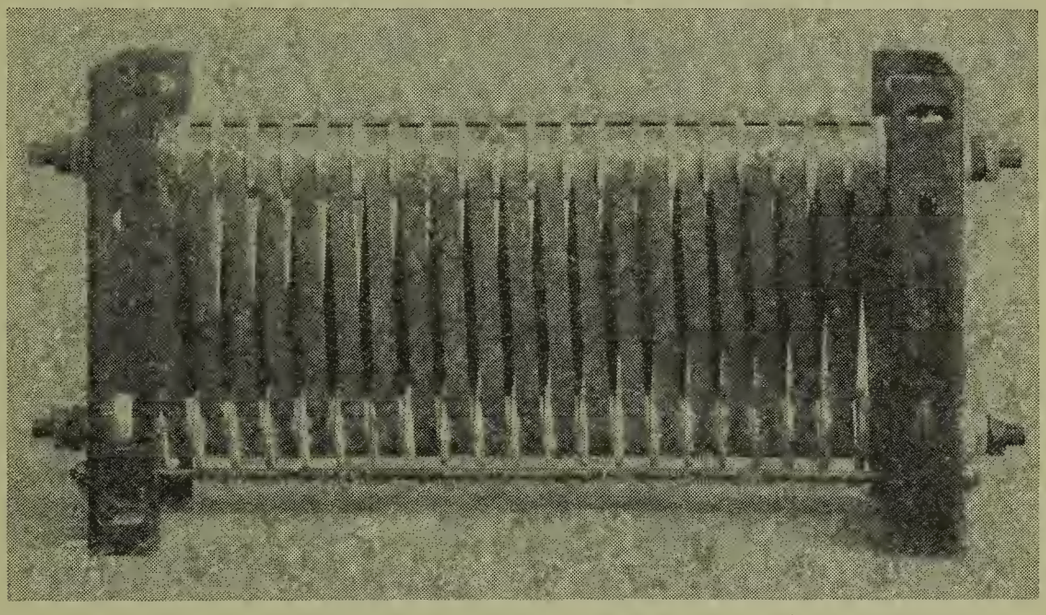


FIG. 1. Oven heater, 2.5 Kw., 110 volts, 21 inches long, 10 inches high, 6 inches deep. Connected in series for any voltage up to 550 volts, and arranged for balancing on two or three phases. With special insulated supports, these heaters have been used on 1200 volts for railway armature baking.

from the inside to the outside of the oven, which in many cases accounted for 50 percent of the entire radiation loss. This, in course of time has been reduced to a large extent, consistent with good mechanical construction.

Electrical manufacturers began to appreciate the difficulties encountered in oven work, and to design heating elements specially adapted to ovens. Approximately 95 percent of all electrical troubles occurred in the terminals or connectors. Copper wires were first used to connect the heaters, the method for making the connections being left largely to the skill and imagination of the electrician doing the work. Bus bars were substituted for

wire, aluminum bus bars for copper, and finally cold rolled steel bus bars were adopted, which has now become standard practice.

In adopting the cold rolled steel bus bar construction, an important step was made in the development of the heater, by a design which permitted the bus bars to be mounted directly on top of the heater, on insulators, attached to the heater frame, and having standard cold rolled steel connectors of sufficient shapes and combinations to permit an installation of the complete equipment within the oven by a workman using only a wrench.

One of the most important developments was that of automatic temperature control for the ovens. Magnetic contactors were in use in connection with the operation of motors, and were first used in connection with ovens as remote controlled circuits, using "on" and "off" push button stations inserted in the magnetic coil circuit. Mercury and vapor tension thermostats were in use for indicating temperature or ringing alarm bells, to which were added adjustable "high" and "low" contact hands, controlling the temperature through definite limits. Suitable relays were added so that the "making" or "breaking" of the high or low contact on the thermostat would cause the main magnetic contacts to open or close, as the case may be, depending upon the temperature within the oven.

Small ovens, 100 Kw. capacity and under usually have the heaters all placed on one circuit, which is automatically controlled. In many installations, and particularly in larger ovens the heaters are divided into two or more circuits, one of which may be a constant heat circuit not actuated by the thermostat, and of slightly less than sufficient capacity to maintain the radiation and ventilation losses, or in other words, to maintain the operating temperature without any work in the oven. The rest of the heaters are placed on a temperature control circuit, and are cut on and off automatically as may be required to maintain uniform temperature.

Natural ventilation was used entirely with gas ovens, and for a considerable time with electric ovens. It was found, however, that on certain days a longer length of time was required for baking than on others, and investigation showed this to be due to atmospheric conditions. Investigations also showed that many explosions of gas ovens had occurred on such days, as the result

of insufficient ventilation. In ventilating electric ovens from the roof, 20 changes of air at room temperature was figured as sufficient, but later when using the floor method of ventilation 10 changes of air at oven temperature was estimated to be sufficient to keep the volatile gases sufficiently dilute to prevent explosions.

With atmospheric conditions affecting the amount of air entering the oven, it was necessary to provide positive means of insuring a definite amount of ventilation at all times. Furthermore, it was difficult for oven builders to design the ventilating system so as to give the required number of changes of air per hour, the tendency being to err on the safe side, with the result that in most cases, under normal conditions, an excess amount of air was entering the oven, causing an excessive loss, and low efficiency of operation. To provide for these conditions, motor driven exhaust fans were used for exhausting a definite amount of air per hour from the oven, insuring positive ventilation, provided the exhaust duct remained open to the atmosphere at all times.

In the baking of enamels, there is given off, in addition to the volatile vapors, a vapor containing oil and asphaltum compounds, in the form of a brown smoke. A tarry substance condenses from this vapor upon reaching a temperature below its distillation point, which is usually at some part of the vent duct external to the oven. This substance solidifies, cokes, and in course of time will gradually fill up the duct unless means are taken for keeping the ducts clean. The gradual restriction of the cross section does not become apparent, and has resulted in many disastrous explosions.

In order to eliminate the possibility of explosions due to vapors condensing and solidifying in the vent ducts, a system has been perfected which, in connection with a motor driven exhauster, automatically shuts off the power the instant the exhaust duct becomes restricted in any manner, or in the event the runner of the exhaust fan becomes loose on its shaft, as happened in one case.

When electrically heated ovens first came into use, gas ovens were being operated at temperatures from 300 to 350° F. (149° to 176° C.), and the baking period was from 3 to 4 hours. With electric ovens the baking period was reduced to less than one-half, and with enamels baking at 450° F. (232° C.) the baking period was

reduced to one hour, and in some cases to 30 minutes. However, too short a bake is injurious to the enamel, since the vapors are driven off too quickly, not allowing the enamel sufficient time to flow smoothly, also causing craters, due to the rapid expulsion of the vapors, which craters do not have time to heal over before hardening.

In the proper baking of enamels, it is essential that the work and the enamel be heated uniformily, hence the larger the mass the slower it should be brought up to its maximum temperature. Enamel on being heated softens and tends to flow. In fact, it will flow excessively if the heating is done rapidly. A certain amount of softening is essential to produce a smooth finish, but actual flowing and dripping of the enamel off the work should be avoided, since that is not only a waste, but results in lumps being formed at the points where the dripping takes place.

Two things are essential in the baking of enamels, a uniform protective coating of enamel, and maximum adhesion between the enamel and the work. The greatest amount of adhesion and the thickest and smoothest surface of enamel is obtained when the work is heated at such a rate as will permit the metal to become uniformly heated at the same rate as the enamel on its surface. Many defects in enameling are traceable to ignoring or being in complete ignorance of this fact.

Much trouble is experienced by manufacturers of automobile fenders, with the rivets and heavy rims coming out of the oven bare or only partly covered. The cause is usually attributed to oil or grease and to improper cleaning, and after more thorough cleaning of the parts, it is found that the trouble has not been appreciably remedied, the bare spots having to be touched up by hand. The real cause is due to the work being run into a hot oven or subjected too rapidly to a high temperature, the sheet metal heating up rapidly but the rivets and heavier parts lagging in temperature sufficient to permit the enamel to flow entirely off that part.

In one installation, where a continuous conveyor type oven was used for fenders, the work had been coming out of the oven with practically all the rivets bare. There were also bare spots on the sheet metal. These bare spots had been attributed at first to improper cleaning of the fenders, but after trying many remedies

it was evident that the trouble was due in some way to the heating process. An investigation of the oven while in operation revealed the cause of the bare spots on the sheet metal work.

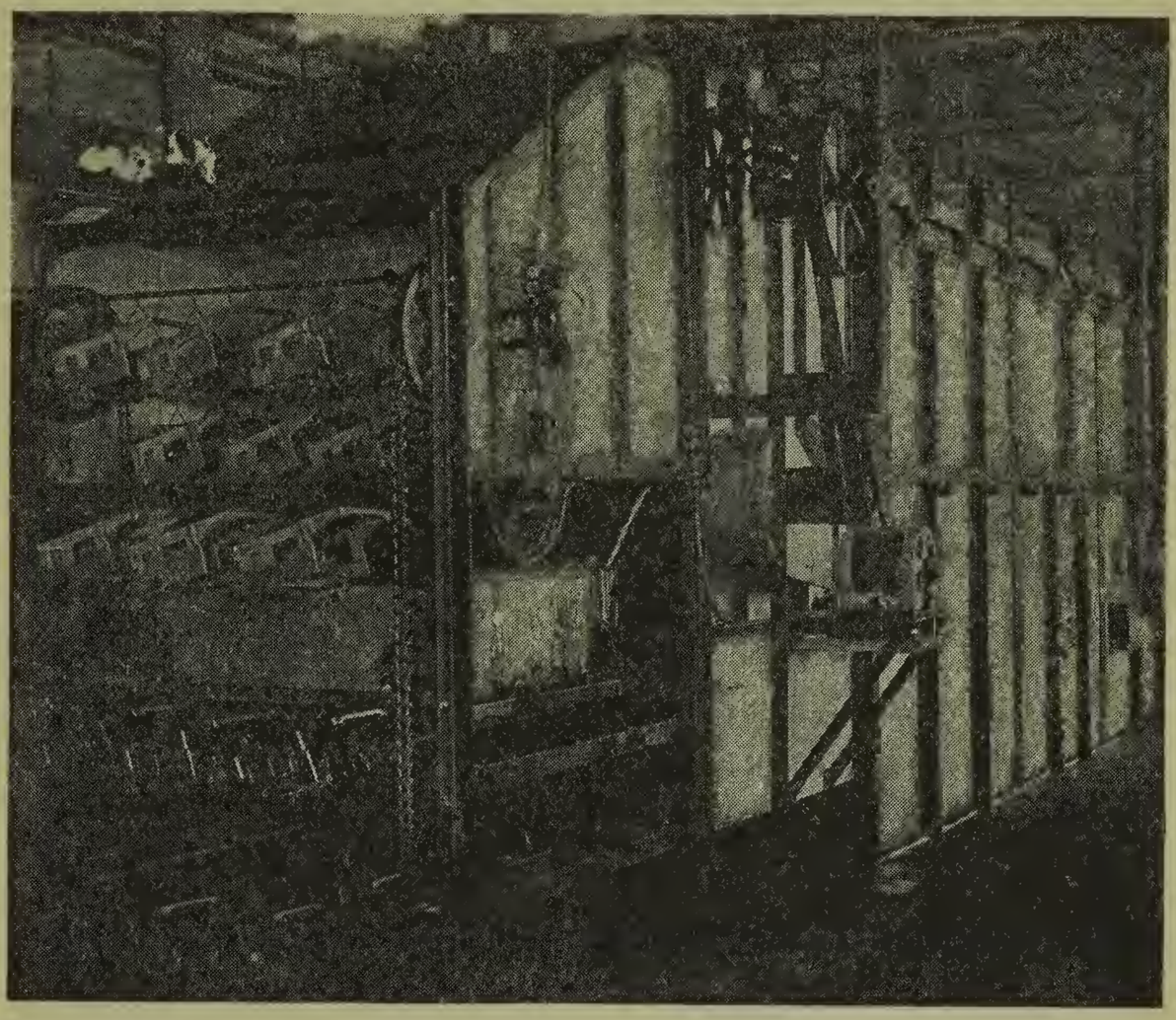


FIG. 2. A continuous conveyor type electric oven. Suitable for baking enamel on typewriters, fans, small motors, automobile license tags, small castings and sheet metal work of various sizes and shapes. The work is hung on the conveyor, and is carried over a pulley down into a tank filled with enamel, up and down through a dripping space and then through the oven. The conveyor travels in an up and down direction as it progresses through the oven, returning near the floor and under the heaters. In the illustration, three rods of the conveyor are shown filled with typewriter frames before they have been dipped, and two rods after the frames have been baked and are coming out of the oven. Automatic temperature control is essential to the successful operation of this type of oven.

The oven was of the elevated tunnel type, with an approach rising to a height of approximately 8 feet, in a distance of 15 feet. Ventilation was accomplished at the floor line, one outlet being half way up the approach, one at the end, and one in the center of the oven. The heavy tarry vapors were being drawn into the

unheated approach, where the walls were found to be covered with the condensate, showing that the walls were at a lower temperature than the vapor. The condensate on the ceiling was dripping down on the work, and wherever it struck, the enamel was washed off clean.

A horizontal approach 20 feet long was added to the inclined approach, and one-third of the heaters taken out of the oven and placed in the inclined approach, producing a long preheating chamber and a baking chamber. The first batch of work coming through the oven after this change not only had no bare spots on the sheet metal work, but every rivet on the fenders was perfectly covered with enamel. The proper preheating of the work had solved the problem entirely.

In another instance where a semi-continuous conveyor oven was used, the work was run immediately into a hot oven, the baked work passing out the opposite end as the green work entered. The oven temperature dropped from 450 to 300° F. (232° to 149° C.) while the change was being made, due to the rapid absorption of the heat by the work. A bake was obtained in 35 minutes. Practically 50 percent of all rivets on the fenders came out bare. So many fires and explosions had taken place in the ovens that if an alarm was turned in, the works fire department immediately made a dash for the enameling department without looking to note on the indicator the location of the fire, feeling sure that the ovens were on fire again.

As soon as the baked work was run out of the oven, it was taken off, dipped, and hung back on the conveyor for the second baking. The last pieces were finished at about the time the bake in the oven was completed, consequently, the work did not have sufficient time to drip before entering the oven. To make matters worse, heaters had been placed on the floor, in addition to those along the sides, in order to accelerate the rate of baking. The heaters were covered with baffle plates, but the green enamel dripping on the hot plates took fire readily.

The explosions were due to driving off the volatile gases too fast for the vent ducts to handle them properly. The naphtha vapors begin to come off at room temperature, and for best results, should be entirely liberated by the time a temperature of 250° F. (121° C.) has been reached. Therefore, it is evident, if the work

is placed immediately in an oven having a temperature of 450° F. (232° C.) and the heat turned on, the gases will be generated at an enormous rate.

The difficulties above experienced were entirely overcome by removing the heaters from the floor, lengthening the bake to 50 minutes, and not turning on the heaters until after the work had been in the oven for 15 minutes. By the end of that time, the oven had dropped to a temperature of 225° F. (107° C.), and all the volatile gases had been driven off with entire safety. The work also had 15 minutes longer to drip outside the oven. The

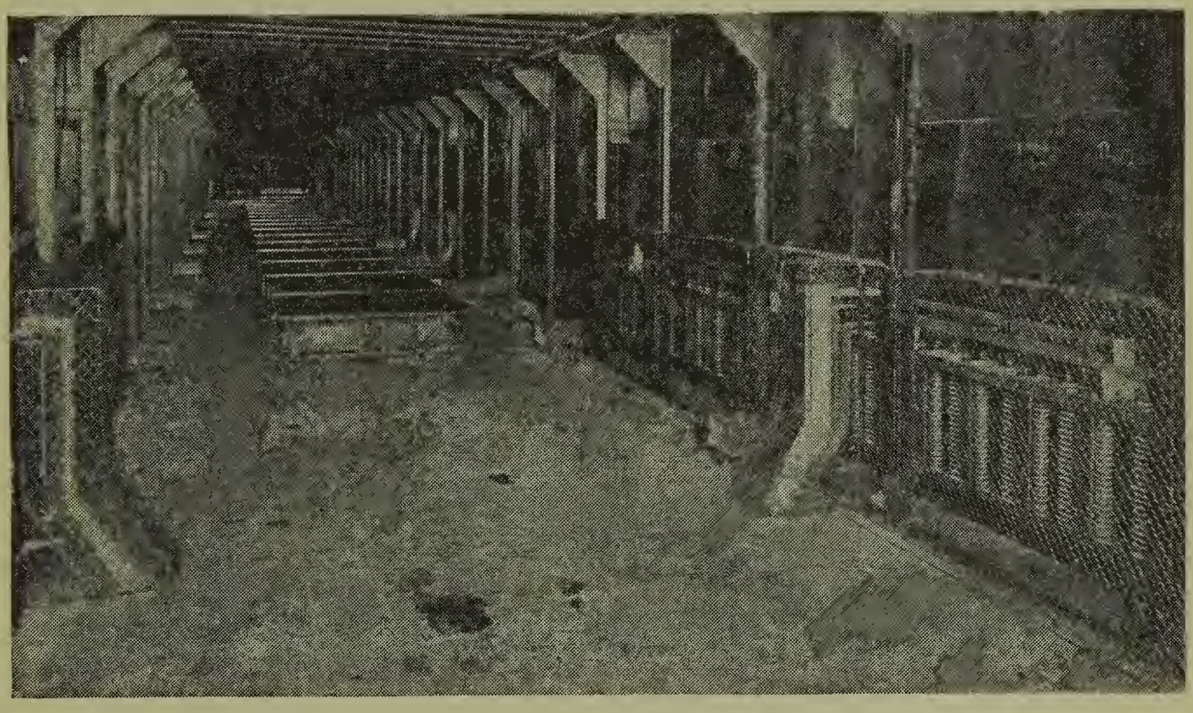


FIG. 3. Interior view of one of the ovens of the Cadillac Motor Car Co. Note vent ducts on floor, projecting out from sides.

net result was the elimination of fires and explosions; the preheating allowed the enamel to adhere properly to the rivets; less enamel flowed off the fenders, due to greater length of time allowed for dripping and setting of the enamel in the air, also due to preheating; the finished product had a much smoother and higher gloss finish.

The electrification of enameling ovens has permitted the liberation of an enormous amount of heat in an oven in a very short period, consequently, with the necessity for production confronting the user, he is apt to attempt to speed up the baking operation to the limit. The man responsible for the capacity and type of

equipment being installed may not have sufficient information in connection with that particular plant operation to predict exactly the results finally obtained. For this reason it is not sufficient to convince a customer that he should purchase electrically heated ovens, and obtain his order, but it is even more essential that an inspection be made of the installation when in operation and results obtained, for the purpose of assuring the success of the entire operation.

Before the adoption of electric heat, oven operations were practically limited to batch processes, due to the difficulty in controlling the temperature, securing and maintaining the correct temperature distribution. The use of electric heat has been responsible for the development of continuous conveyor type ovens of all types, shapes and forms to fit in best with a manufacturer's particular process or location.

The installation of electric ovens at Cadillac Motor Car Co., Detroit, Mich., is an example of the development of the art of baking enamel on automobiles, and is a tribute to the work of the pioneers in industrial electric heating. This magnificent installation also shows the confidence of a large automobile manufacturing company in the superiority and economy of electric heating.

The ovens are designed for a capacity of 100 cars per 9 hour day, 26,000 pounds (11,793 kg.) of work being baked in four ovens each hour. The ovens are the continuous conveyor tunnel type, elevated so as to allow an inclined entrance and exit to give an air seal at each end. The work is hung on the conveyor, is dipped automatically in enamel, and passes through four ovens in succession, the dipping each time being done automatically.

In the first half of each oven, the heaters are placed along the side walls, and approximately three-fourths of the total amount of the air required for ventilation is exhausted from this section, at the floor line. In the second half of the ovens heaters are placed on the floor, the ventilation in this portion being partly from the floor near the side walls, and partly from the ceiling. Heaters along the side walls are protected by wire screen, and those on the floor by sheet metal baffle plates, in case any pieces of work should fall off the conveyor in passing through the oven.

The amount of air required for ventilation in each oven was accurately determined as follows: Samples of the enamel were

analyzed to determine the amount of solvent present. A definite amount of solvent vapor and air was injected in a small test oven, completely filling it, and attempts made to ignite it by means of an arc from a spark plug placed in the center of the oven. The reasons for using an arc as a basis for these tests is based on the fact that in any electrical installation, an arc is apt to occur, and should that condition exist, it is essential that the gas mixture within the oven be sufficiently lean to make an explosion or fire impossible.

It was found that a mixture of 92 percent air and 8 percent sol-

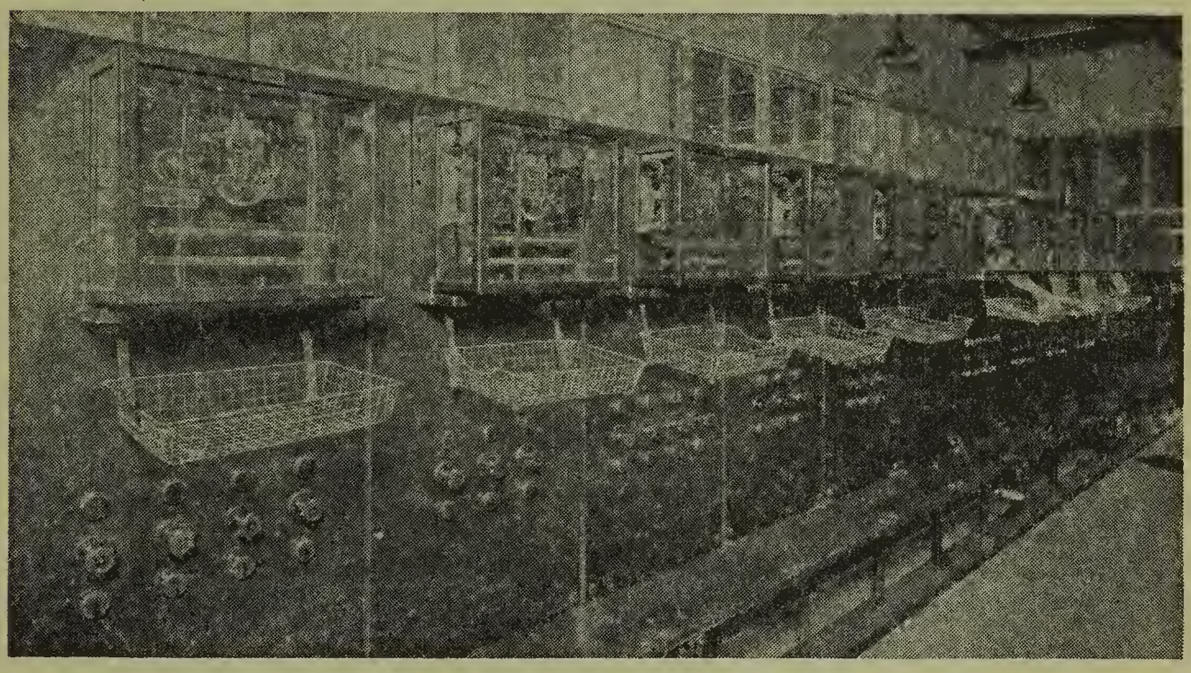


FIG. 4. Temperature control panel, from which point the constant heat and temperature control circuits are operated. Switches with red and green lamps indicate when each circuit is on or off. The instruments shown are on the temperature control circuits.

vent vapor (both percentages by weight) would cause an explosion of a mild form. A mixture of 93 percent air and 7 percent solvent vapor would take fire but not explode. A mixture of 94 percent air and 6 percent solvent vapor could not be made to take fire. Allowing for an ample factor of safety, a mixture of 95 percent air and 5 percent solvent vapor was recommended. As the percentages of solvent vapor increased, the explosions increased in violence until they reached a maximum with 85 percent air and 15 percent solvent vapor. Increasing the solvent vapor beyond this point, the explosions became less violent due to

a resultant rich mixture, but it was found that in such cases, the amount of oxygen present in the air was not sufficient to oxidize the enamel in baking.

Each oven is 12 ft. (3.6 m.) wide and 8 ft. (2.4 m.) high. The conveyor travels at a speed of 2 ft. (60 cm.) per minute. The maximum temperature in the baking zone of the oven is held constant at 450° F. (232° C.) Heaters are arranged to give a gradual rise of temperature up to the maximum required.

Oven No. 1 is 84 ft. (25.6 m.) long over all, equipped with 156 heaters giving a total capacity of 390 Kw. Two constant heat and two temperature control circuits are used.

Oven No. 2 is 114 ft. (34.7 m.) long over all, equipped with 168 heaters, giving a total capacity of 420 Kw. One constant heat circuit and three temperatures control circuits are used.

Oven No. 3 is an exact duplicate of oven No. 2.

Oven No. 4 is 134 ft. (40.8 m.) over all, equipped with 180 heaters, giving a capacity of 450 Kw. One constant heat circuit and four temperature control circuits are used.

DISCUSSION.

C. G. SCHLUEDERBERG[1]: Has electric superseded gas equipment entirely, or to what extent?

WIRT S. SCOTT: I would say that it has superseded it 90 per-cent, roughly speaking. Practically all large installations are of the electric type. There has been a state of progressive development, and during this time it has been a race between the gas and the electric manufacturers' equipment.

I just received word recently that a large gas installation is being made in Lansing, Mich., in the Oldsmobile plant. They are claiming many advantages over the electrical installation. Whether that is true I do not know.

[1] Asst. to Manager, Supply Dept., Westinghouse Elec. & Mfg. Co., E. Pittsburgh, Pa.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 22, 1922, Vice-President Crosby berg in the Chair.

FIRING OF CERAMICS IN ELECTRIC FURNACES.[1]

By E. L. Smalley[2]

Abstract.

Properly designed electric furnaces are dependable for ceramic firing at temperatures up to 1100°C. Grinding wheels have been produced by the use of the electric furnace in a shorter time and of greater wearing durability than is possible in the kiln process. The cleanliness of atmosphere, the uniformity of temperature control and other features of electric furnace operation have made it very adaptable in the automobile and china industries, and in the manufacture of glassware and bi-focal lenses, where substantial reduction in the percentage of rejects has been experienced.

[A. D. S.]

The application of electric furnaces in the ceramic industries affords an opportunity for the betterment of the product, to an extent not less remarkable than the achievements in the metal industries. The perfect control of temperature, cleanliness of atmosphere, and even distribution and uniformity of temperatures have shown in industrial applications on a large scale that the electric heat is practical and gratifying in this field.

In the making of grinding wheels the electric furnace of the metallic resistor type has helped to eliminate the slow and antiquated method of using kilns. Wheels have been pressed and burned and operated in one working day. A wheel so made, and subsequently tested in the regular production work in an automobile plant, ground a number of pieces equal to three hundred percent of the number of pieces ground on a wheel made by the old kiln process, requiring three to four weeks total time in the

[1] Manuscript received August 4, 1922.

[2] Manager of Electric Heating Apparatus Co., Newark, N. J.

making. Not all the credit for this performance can be claimed for the electric furnace as the wheel fired in the electric furnace was manufactured by a special process. But the manufacturer of such wheels states that the electric furnace makes his process possible, and it was upon his recommendation that a Detroit automobile manufacturer has installed an electric furnace for vitrifying that type of grinding wheels.

The temperature required for the vitrifying process was not in excess of 1100° C., and plans are now being perfected for a continuous process electric furnace for burning these wheels. The wheels are of a maximum size of 30 x 6 inches. (75 x 15 cm.)

The electric furnace in this instance will occupy a floor space not over ten percent of the space required where wheels are in process of making for three to four weeks by the kiln process.

The china industries are likewise benefited. One of the largest manufacturers of the highest grade of china in Trenton has proved the entire adaptability of metallic resistor furnaces for his color firing, at temperatures up to 1050°C., such as is required for chrome blue. He reports that desirable color tones are secured in the electric furnace that are impossible in fuel furnaces.

In one test run made by the Trenton manufacturer an electric furnace 32 inches wide by 48 inches deep by 16 inches high, (80 x 120 x 40 cm.) was charged with 104 dinner size plates. Plates of various colors and color tones, including gold, were selected so that a temperature of 740°C. would be satisfactory for all. The plates were stacked on cast iron setters. Seger cones of two consecutive numbers were placed at every conceivable position throughout the furnace chamber wherever it was thought possible that a slight temperature difference might exist. All cones of the same fusion number were uniformly fused. All colors were perfect.

In addition to the seger cones, each setter of each plate supported a small "color-test" piece. These test pieces all bore the same color, which would disclose a different temperature if any variation in shade or tone of color existed after firing. All the test pieces disclosed the same shade or tone after firing.

Commercial glassware can be annealed electrically to a perfection not possible in any fuel-fired furnace. The success of such an electric furnace installation depends upon the correct form of

furnace combined with a suitable method of handling. One glass manufacturer installed a furnace for annealing goblets and fruit jars. The furnace was 22 inches wide by 120 inches long by 60 inches high, (55 x 300 x 150 cm.) and was fitted to an over-head I-beam conveyor already installed for handling the ware. An attempt had been made to use the conveyor for annealing by natural gas but without success.

It was shown that the conveyor was impractical on account of excessive heat losses where the conveyor was in contact with the furnace, but the remarkable annealing effect of electric heat was fully attested. Sixty-five test goblets were taken at random from the top, bottom, sides and centers of the several trays of the conveyor supporting the goblets. The goblets were subsequently tested in a spectroscope. Sixty-four were A-1 grade, showing no internal strains; the sixty-fifth goblet was B-1 grade. Grade C-1 was considered a passable grade. The electric furnace is therefore worthy of serious consideration especially in view of the declining supply of natural gas, and the almost inevitable decline in electric power costs.

In the manufacture of bi-focal lenses, electric furnaces have reduced the percentage of rejects and losses from 18 to 20 percent in gas furnaces to 2 or 3 percent in the electric. Rejects and losses in the gas furnaces were due to oven-fusion, cracking, lack of complete fusion, and internal strains. Losses in electric fusions are due principally to inherent defects in the lenses. The saving has been effected due to the cleanliness of the atmosphere; to the uniformity and control of heat, and to the ability of the electric furnace to produce a tapered heat where required.

At the plant of a manufacturer in New York State, sixty furnaces are installed for the fusing of bi-focal lenses. The critical heat of fusion is about 775°C., and a tapered heat is necessary to prevent rupturing the lenses which would occur with heat too suddenly applied. All of the sixty furnaces are about 8 inches wide by 5 inches high and 14 to 18 inches long, (20 x 12.5 x 35 to 45 cm.) arranged in 15 batteries, each battery consisting of four furnaces to form a combined length of about 72 inches (180 cm.) per battery.

The lenses are set on plaques, four to a plaque, and conveyed continuously through the furnaces. The two furnaces at the

entering end are equipped with one automatic temperature control. Each of the last two furnaces of the four in the battery are similarly equipped. As each battery of furnaces turns out approximately $1800 worth of lenses per day, the saving of about 16 percent in the reduced losses, is large interest on the investment.

The improper application of electric heat should be carefully guarded against. The release of heat must be from the correct direction with respect to the charge. It must be so distributed in its source that no overheating at any part will result. The more surface of the heating chamber covered by a source of heat, the more successful will be the application.

Electric furnaces as constructed today, when properly selected as to their design, are entirely dependable for ceramic firing at any temperature up to 1100°C.

DISCUSSION.

L. E. SAUNDERS[1]: I think it is a little unfortunate that Mr. Smalley, who is engaged in the making of heating apparatus, should so seriously promote a process which he mentions in the opening of his paper, and which has not reached its commercial status. Claims are made there which are quite remarkable, and I fear cannot be generally substantiated.

Mr. Smalley describes a process for making grinding wheels at a lower temperature than has been used heretofore. This process is being experimented upon; wheels resulting from it are still to be tried generally, and certainly no such general outcome has resulted as is indicated at the bottom of the first page.

Please do not think I am trying to cry down a process for making grinding wheels, which can be put into practice at lower temperatures. That is a consummation devoutly to be wished, but such a process, as far as I am aware, has not yet been fully developed.

Grinding wheels of other types than are mentioned here are manufactured commercially on a large scale, and the heating is

[1] Norton Co., Worcester, Mass.

done electrically. The temperatures, however, are very low. The bond materials which are being matured are of organic type, and the temperatures range from 150° to 200° C.

Another type of grinding wheels made in this manner uses silicate of soda as a bond, and the temperatures of baking are not over 250° C. This is also being successfully done electrically.

A. STANSFIELD[2]: From the title of this paper, "Firing of Ceramics in Electric Furnaces," I got the impression of a somewhat high temperature. I should like to ask Mr. Smalley, if he were here, what is the high temperature he contemplates using in these electric furnaces, and what kind of electric heating units he applies. We have had several papers presented here with regard to electric furnaces, but I do not think we have had any information with regard to this type of electric heating.

W. D. BANCROFT[3]: I would like to go at the thing from a slightly different point of view; that is, small scale production. It would be a satisfactory thing, indeed, if we could have a high temperature electric furnace adapted for use in ceramics, especially for making artistic porcelain. As things now stand the losses are large indeed. With a suitable furnace, you could regulate your firing, you could regulate your atmosphere, and you could get results which are not obtained now; and the extra cost of electric heating, which we know is higher, would be covered a great many times over by the increased number of good pieces.

Then there is another side which is even more interesting to me, and that is, if we had a kiln of this sort in which we could make, say, half a dozen pieces at once, it would be practicable for such a kiln to be run by individuals, which would mean that you could get production by artists, and not factory production. It seems to me if we could develop the right kind of furnace, it would open up the possibility of real artistic work in a way which has never been done anywhere. Of course, you must find your artists. However, your artists cannot do anything now, because they must turn things over to be fired in a regular porcelain kiln, and heaven knows how it will come out. You cannot

[2] Professor of Metallurgy, McGill University, Montreal, Canada.
[3] Professor of Physical Chemistry, Cornell University, Ithaca, N. Y.

try experiments or anything like that; so there is a distinct field for small electric furnaces, to be run by individual people, who will make their own designs, and their own vases, and turn them out in small quantities. I am not talking about making dinner sets or anything of that sort, but really artistic pieces.

If that can be done I see no reason why we should not have a regeneration of first-class porcelain, which will be as good as that done by the Chinese in the old days. The Chinese did not have the advantages that we have; they did not have the chemical knowledge; the only difference was that they did have the artistic sense. If the electrochemists will develop the mechanical side, it will be up to somebody to develop the artistic side, and there is a real opening. It does not mean such a tremendous lot in dollars and cents, but it means a great deal in the joy of life.

L. E. SAUNDERS: In answer to Dr. Stansfield's question, I wish to say that this paper mentions metallic resistors going only to 1100° C.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 22, 1922, President Schlueder-berg in the Chair.

ELECTRIC STEAM GENERATORS AND THEIR APPLICATION.[1]

By P. S. Gregory[2]

Abstract.

The water-resistance electric steam generator consists essentially of a closed pressure vessel, to which is connected a source of water supply and from which water may be drawn off at the bottom and steam at the top. In this vessel electric energy is made to flow through the water from an electrode in the form of a plate or tube, to the shell of the vessel, or to the metallic inner lining. Alternating current energy is used at a pressure varying from 110 to 12,000 volts. The generators are constructed for the use of three-phase power, either by employing three electrodes in one vessel or by the use of three vessels with one electrode in each, in which case the outer shells are connected together in star. In this type of generator there is no heating surface, the generation of steam taking place throughout the water, and, as a consequence, no portion of the apparatus is at a higher temperature than the temperature of the steam. This is a most important feature from the viewpoint of safety and continuity of operation, as can be readily appreciated.

The chief advantages of the water-resistance type of steam generator over the metallic resistance type are freedom from electrical and mechanical troubles, ease of regulation and cheapness.

There are in operation in Canada and in the United States at the present time installations of electric steam generators totaling about 150,000 kw., which are for the most part installed in paper plants. [C. G. F.]

[1] Manuscript received August 22, 1922.

[2] The Shawinigan Water and Power Co., Montreal, Canada.

The subject dealt with in this paper is the commercial application of electric energy for the production of steam by means of the water resistance type of electric steam generator.

The production of steam by means of electric energy is not a new process, and the water resistance type of electric steam generator has been in use in Europe for some fifteen years, though in the majority of installations in small sizes only, of 1,000 Kw. or less.

In general the cost of electric energy is such that it cannot be used commercially for the production of steam, but there are circumstances under which the conversion of electric energy into steam, even on a large scale, becomes economically feasible. The required conditions are a surplus amount of electric power, for which there is no other use at certain times, or a cheap supply of power. One or other of these conditions frequently exists in industrial plants. All manufacturers who purchase their power on a flat rate basis have at certain times in the day, or on certain days in the month, power available for which they have paid under their contract, but of which no use is made. The saving of coal which can be effected by the conversion of such surplus power into steam is a subject worthy of careful consideration. In the case of the existence of a cheap supply of power, the price which can be paid for this energy for the purpose of the production of steam is of course dependent upon the price of coal, and can readily be calculated.

The fundamental relationship between electric energy and heat energy as pertaining to the production of steam may be stated as follows: One Kw.H. is equal to 3,412 British thermal units. In order to produce one pound of steam at a gauge pressure of 100 lb. per sq. inch, from feed water having an initial temperature of 150° F., 1,070 B. t. u. are required. Therefore, if the conversion of electric energy into steam can be made at an efficiency of 97.5 percent one Kw.H. will produce 3.1 pounds of steam at the above conditions of temperature and pressure.

Under average conditions 1 pound of coal in a boiler will produce about 7.5 pounds of steam and therefore, the electric energy which is equivalent to one ton of coal is $15,000/3.1 = 4840$ Kw. H. This is equivalent to approximately 200 Kw. for 24 hours, so that for each ton of coal per day to be replaced by electric energy,

about 200 Kw. of electric steam generator capacity is necessary. On the basis of 4,840 Kw.H. being equivalent to one ton of coal, which is valued at say $8 under the boiler, the price which could be paid for electric energy would be 1.65 mills per Kw.H. If therefore, a supply of power is available at a price not greater than 1.65 mills per Kw.H. in a plant where coal costs $8 per ton or more, the production of steam by electric power is commercially feasible.

The water resistance electric steam generator consists essentially of a closed pressure vessel to which is connected a source of water supply, and from which water may be drawn off at the bottom and steam at the top. In this vessel electric energy is made to flow through the water from an electrode in the form of a plate, or tube, to the shell of the vessel, or to the metallic inner lining. Alternating current energy is used at a pressure varying from 110 up to 12,000 volts. The generators are constructed for the use of 3-phase power, either by employing three electrodes in one vessel, or by the use of three vessels with one electrode in each, in which case the outer shells are connected together in star. In this type of generator there is no heating surface, the generation of steam taking place throughout the water, and as a consequence no portion of the apparatus is at a higher temperature than the temperature of the steam. This is a most important feature from the viewpoint of safety and continuity of operation, as can be readily appreciated.

The chief advantages of the water resistance type of steam generator over the metallic resistance type are freedom from electrical and mechanical troubles, ease of regulation and cheapness. This type of generator has recently been further developed and made applicable to conditions on this continent by Mr. F. T. Kaelin, chief engineer of the Shawinigan Water and Power Co. Units of Mr. Kaelin's design, manufactured by the Dominion Engineering Works, Limited, Lachine, Que., and the Electric Furnace Construction Company, Philadelphia, Pa., are in operation up to 25,000 Kw. capacity. A full description of this type of generator is given in Mr. Kaelin's paper, read before the Montreal section of the Society of Chemical Industry, the Engineering Institute of Canada and the Canadian Institute of Mining and Metallurgy, on January 19, 1922. A low voltage type of water

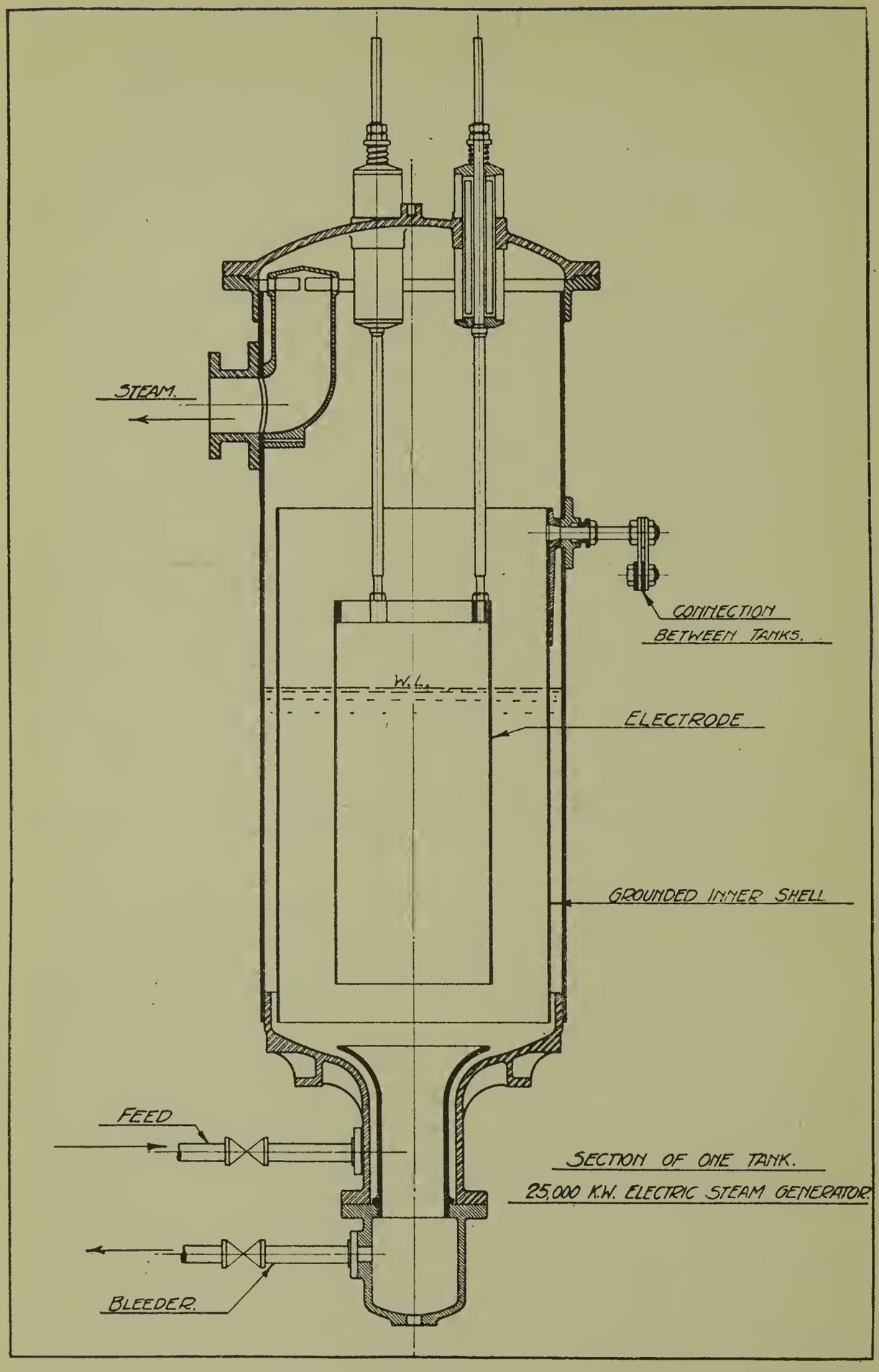

STEAM.
CONNECTION
BETWEEN TANKS.
W.L.
ELECTRODE
GROUNDED INNER SHELL
FEED
BLEEDER.
SECTION OF ONE TANK.
25,000 K.W. ELECTRIC STEAM GENERATOR.

FIG. 1

resistance generator was described at the fortieth general meeting of the American Electrochemical Society in October, 1921, by Messrs. Lidbury and Stamps.[3]

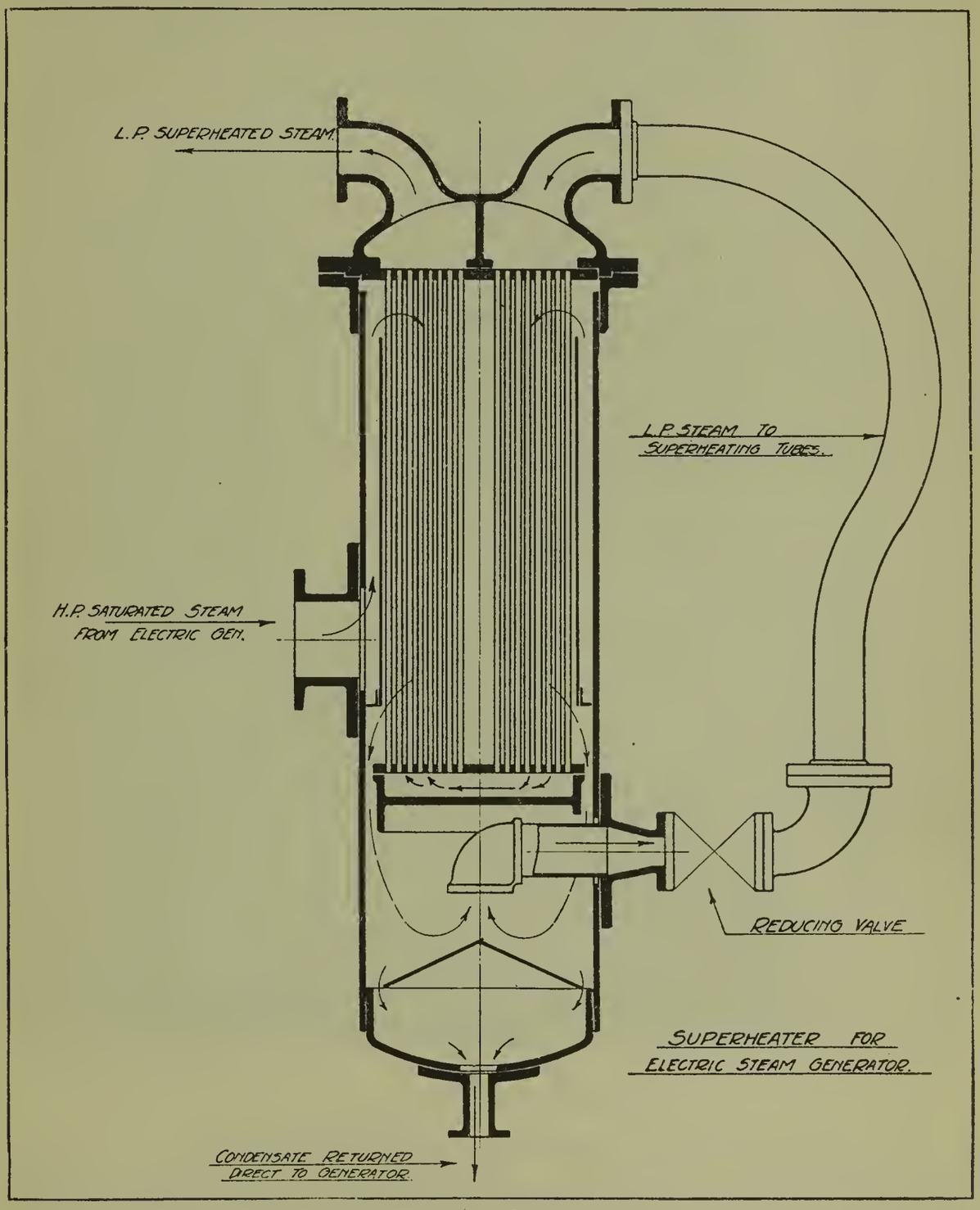
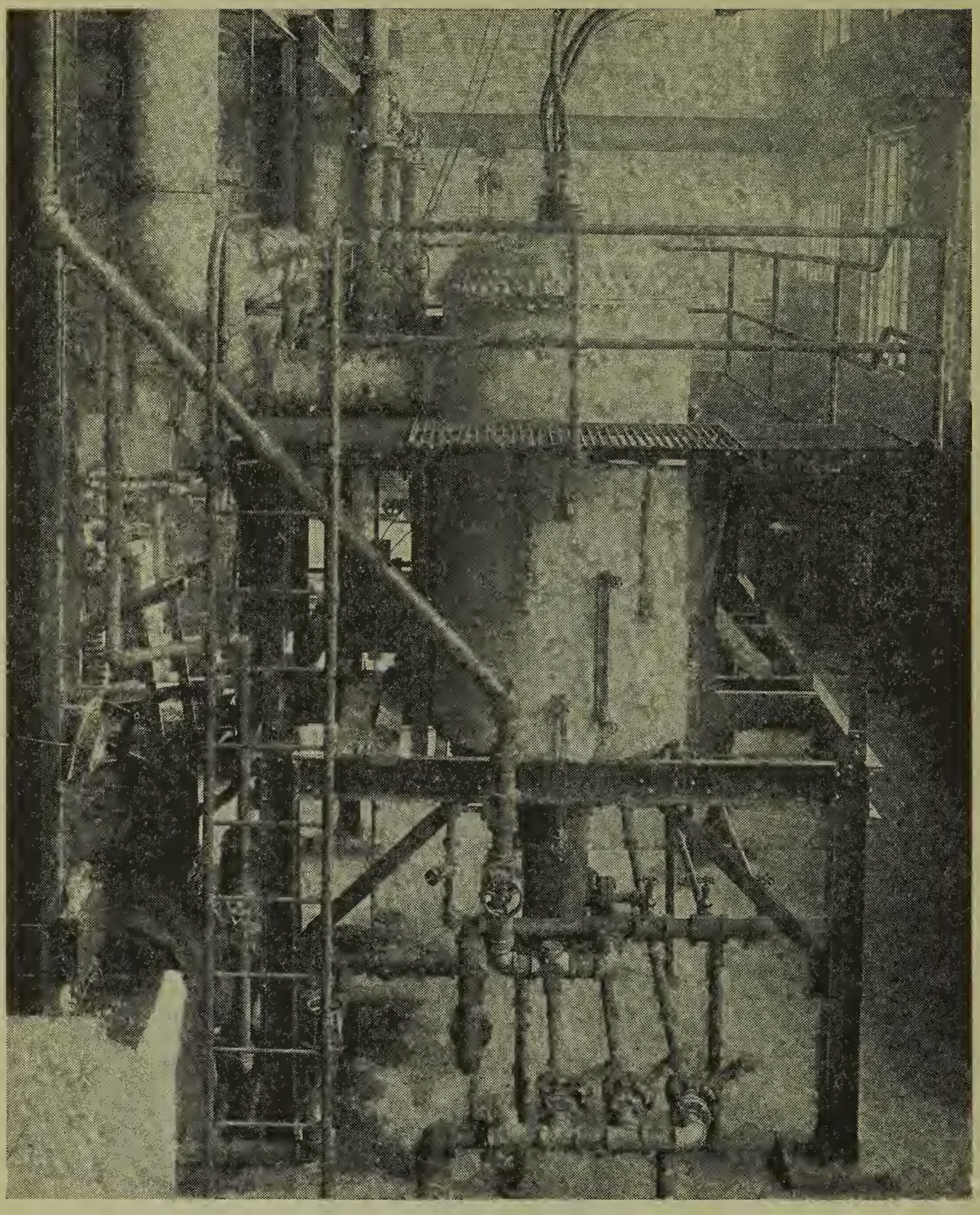

L.P. SUPERHEATED STEAM.
L.P. STEAM TO SUPERHEATING TUBES.
H.P. SATURATED STEAM FROM ELECTRIC GEN.
REDUCING VALVE
SUPERHEATER FOR ELECTRIC STEAM GENERATOR.
CONDENSATE RETURNED DIRECT TO GENERATOR.

FIG. 2

In the operation of this type of generator the load or electrical input is dependent directly upon the area of electrode immersed in water, and inversely upon the resistance of the water. The variation of the water level or the area of immersion is effected

[3] Trans. Am. Electrochem. Soc , 1921, **40**, 467.



An Electric Steam Generator

by the operation of the valve in the feed water supply line. The resistance of water decreases with temperature, the relation being expressed by the formula[4]

$$R = \frac{C}{\sqrt[5]{T^4}}$$

[4] The Generation of Steam by Electricity, by F. T. Kaelin, E. I. C. Journal, March, 1922.

in which R = ohms per cubic inch, T is the temperature in °C., and C is a constant having a value of about 42,000 for raw river water, and about 87,000 for condensate containing 25 percent of make-up water.

The variation of the resistance of the water is effected by controlling the amount of water bled from the bottom of the generator. This water contains a comparatively high percentage of salts, and is therefore of a low resistance, so that an increase in the amount of water bled from the generator means an increase in the resistance of the remaining water and consequently a decrease in the load.

In actual operation it has been found that for ordinary fluctuations of load, such as are obtained in paper mills, a practical method of operation is to maintain a constant water level, and to vary the output of the generator by varying the resistance of the water by means of a bleeder valve.

There are in operation in Canada and in the United States at the present time installations of electric steam generators totaling about 150,000 Kw., which are for the most part installed in paper plants. One of these units is shown on the previous page.

The accompanying diagrams illustrate the present development of the electric steam generator.

Fig. 1 shows a cross section of one of the three tanks of a 25,000 Kw., 6,600-volt unit. The electrode is supported at three points to give mechanical stiffness. The feed water is deflected around the sides of the tank by the funnel shaped casting shown in the bottom of the tank. It is found in operation that this method improves the circulation of water in the generator, and consequently lessens the tendency to prime. The inner shells are separated from the main walls of the vessel, so that even in the event of an electric arc being established between the electrodes and this inner shell, and damaging the inner shell, no weakening of the outer wall would occur.

Fig. 2 illustrates a super-heater by means of which about 50° of super-heat may be given to the steam. The principle of the super-heater is as follows: Steam is generated at a pressure of 300 lb. and is fed into the super-heater, flowing outside of the super-heater tubes. It is then passed through a reducing valve, which reduces it to 150 lb. pressure, and it is fed into the super-heater

again, passing inside the super-heater tubes and thence to the main steam line. The steam at 150 lb. pressure inside the tubes, being at 366° F., absorbs heat from the 300 lb. pressure steam out-

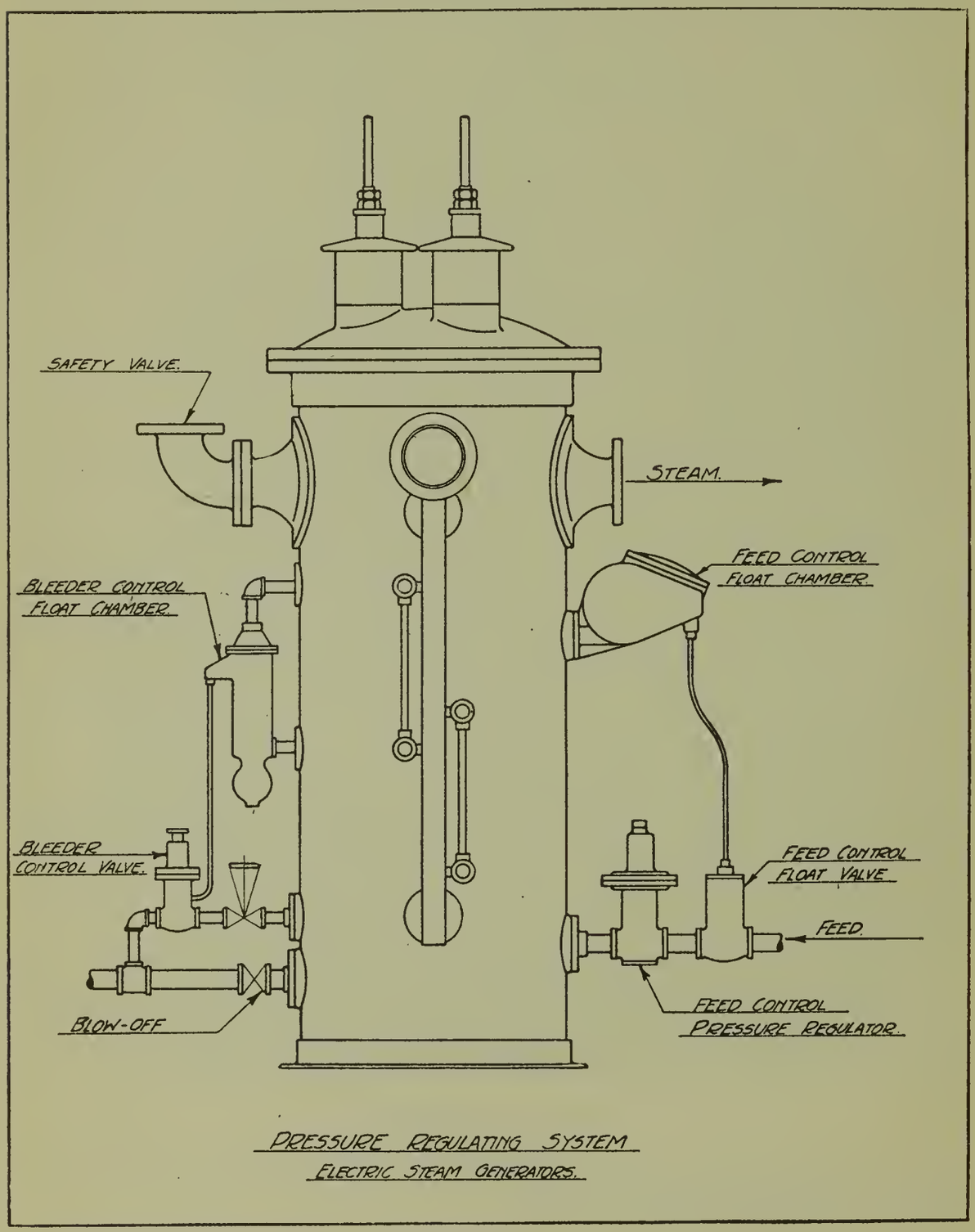


FIG. 3

side the tubes, which is at a temperature of 420° F., and passes to the main steam line in a super-heated condition. The condensate from the super-heater is drained back into the boiler feed. In a super-heater designed to super-heat 20,000 lb. of steam per

hour at 150 lb. pressure from 2 percent moisture to 50° of superheat the total heat to be transferred was 616,000 B. t. u. per hour. The mean temperature difference was 30° F., and the heat transferred per square foot of heating surface per degree temperature difference was 68.5 B. t. u. per hour. The electrical energy required at 90 percent efficiency was 180 Kw. The advantage of this type of super-heater is that the amount of super-heat produced is constant, and that there is no overheating of the superheater in case only a small amount of steam is being drawn from the generator.

Fig. 3 illustrates a generator fitted with a pressure regulating system of control, so that the operation is automatic and no attendant is required. The principle of operation is as follows:

Under normal running conditions the pressure regulator valve on the feed line, which is actuated by the pressure in the generator, is open. If the steam consumption is reduced so that the steam supply exceeds the demand, the pressure will rise, and owing to the operation of the pressure regulator valve in the feed control, the amount of water fed to the generator will be reduced, and the water level in the generator will gradually sink. This may continue until a water level is reached at which the float valve opens in the bleeder line, allowing a quantity of impure high conductivity water to be drawn off from the bottom of the tank. This will have the effect of increasing the resistance of the remaining water as well as still further reducing the water level and therefore of cutting down the flow of current until the supply of steam becomes only equal to the demand, and the pressure regulator valve is operated by the reduction in pressure and opens allowing more water to flow into the generator, gradually raising the water level.

The float valve in the bleeder line is closed by the rising water level, which after one or more cycles of operation will finally attain a position such as, for the particular conductivity of the water in the generator, will produce a steam supply equal to the demand.

If, on the other hand, the demand for steam exceeds the supply, the pressure in the generator will drop, and the pressure regulator valve in the feed line will therefore be opened wide and allow more water to flow into the generator,

raising the water level, and consequently increasing the steam supply until the pressure rises sufficiently to close slightly the pressure regulating valve, adjusting the inflow of water to the outflow of steam.

The possibility of the water level rising too high in the generator is avoided by the high level float valve in the feed line, which shuts off the water supply when the water level reaches the top of the electrodes.

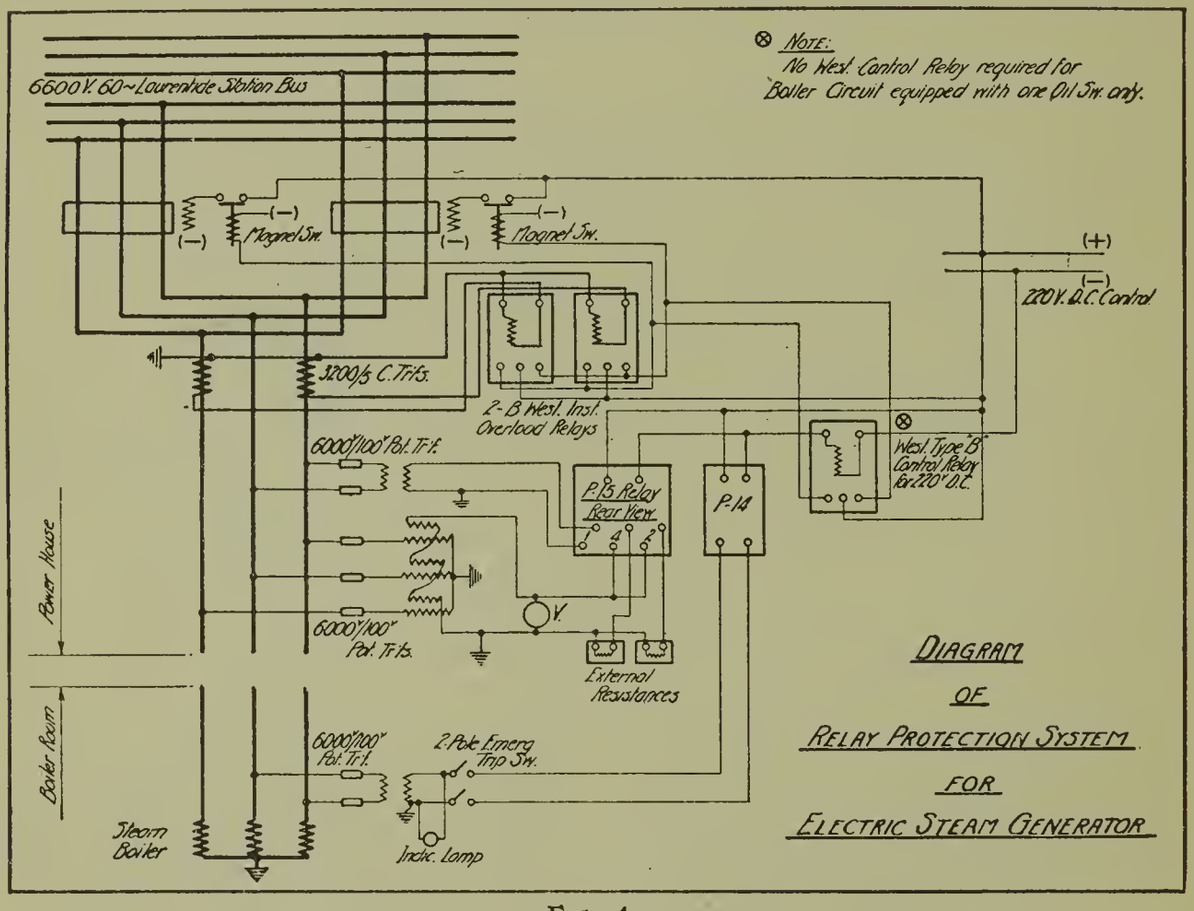


FIG. 4.

A generator fitted with this system of automatic control has been designed to supply low pressure steam for the heating of buildings. As the heating system is a closed system, the condensate being returned to the generator, it was not necessary to install a bleeder control valve on the heating generator.

The development of electric relay systems for the control of steam generators has kept pace with the other developments.

In the operation of the water resistance steam generator, the ordinary bugbear of low water has no terrors, but should an electric arc become established between one of the electrodes and the wall of the vessel, a dangerous condition would at once arise. This

possible source of trouble has been avoided in two ways—by the installation of an inner protective shell separated from the outer wall by an inch or more, and by the development of a potential balance relay system by means of which should a ground occur on

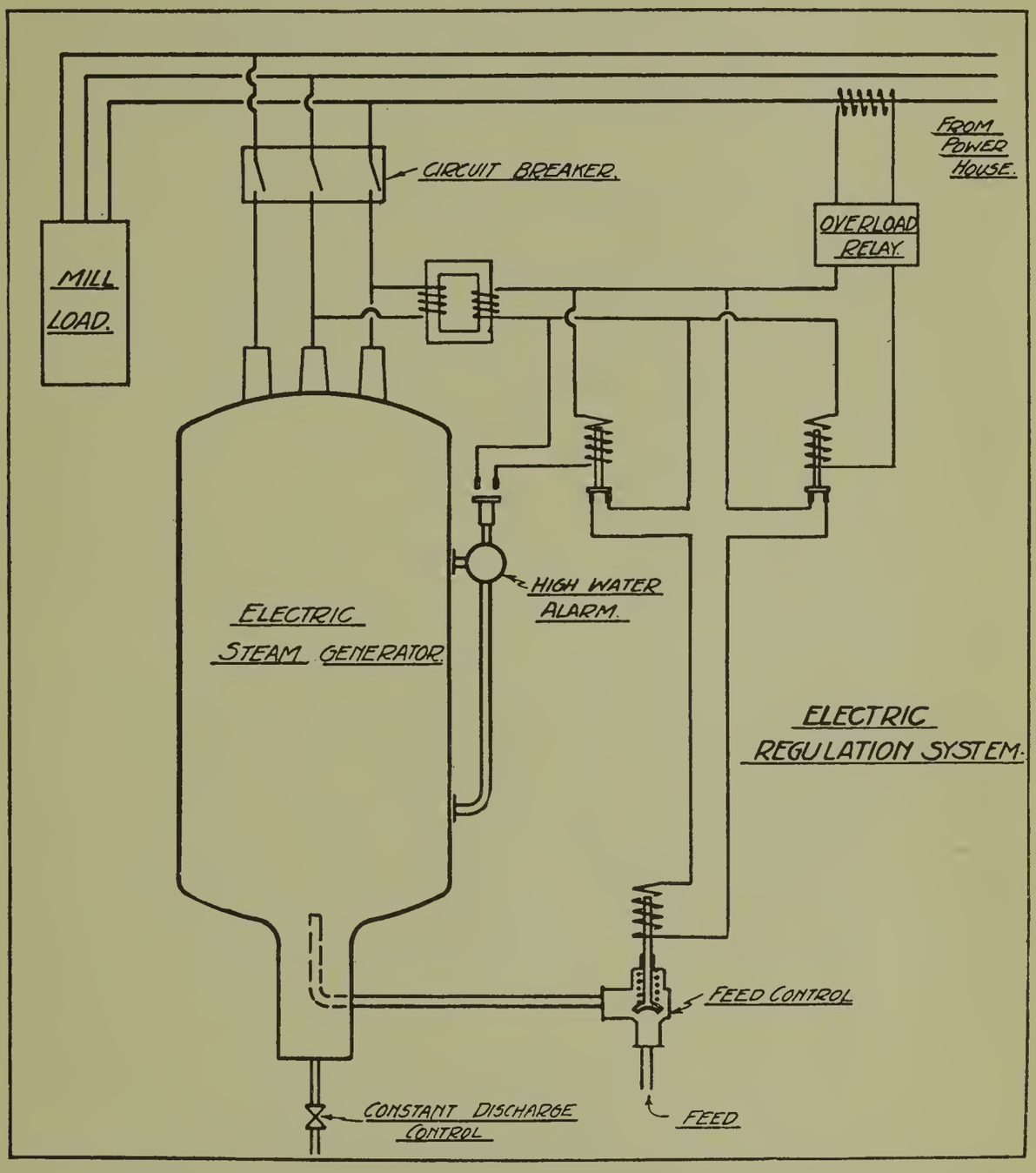


FIG. 5.

any one of the phases, the main circuit breaker is immediately opened. The opening of the circuit breaker does not depend upon the load on the generator, but only upon the potential balance, and the relay will function equally well from no load to full load, which is a very important consideration.

The complete electric relay system installed in connection with

one of the larger units is illustrated in Fig. 4. The relays consist of the ordinary overload relays, the potential balance ground protection relays and an emergency hand-operated relay trip.

In order to make possible the application of the electric steam generator under conditions where a fixed amount of power is purchased, which is not all utilized in manufacturing operations, a relay system has been developed which will govern a total amount of power taken by the consumer, and will insure that all power not otherwise required will be utilized in the electric generator. The relay system is illustrated in Fig. 5.

The principle of operation consists in cutting in or out the feed water supply to the generator by means of the overload relays, which are operated by the total power consumed. The relays are so arranged that once the feed water is cut out it will not be cut in again until the total demand has been reduced some 10 percent below the contract amount. The shape of load curve obtained with a generator controlled by this type of relay system is therefore, saw-toothed, and the relays can be so designed that the amount of available energy which is unused is less than 5 percent of the total energy purchased.

In conclusion it must be pointed out that the water resistance type of electric steam generator has now been developed to such a point that there is on the market today an apparatus suitable for the conversion of surplus electric energy into steam under almost any given conditions. Furthermore, in cases where power is cheap, or where fuel is expensive, or in special industrial processes, the electric steam generator can economically replace the coal-fired boiler.

DISCUSSION.

F. A. LIDBURY[1]: I wish to congratulate the Shawinigan Company and Mr. Kaelin on the success with which they have pursued this line of work. I should like to emphasize the last remark Mr. Gregory made in presenting his paper, namely, that the application of electric steam generation is an individual matter and must be carefully considered in each case, with reference to the conditions.

[1] Works Mgr., Oldbury Electro-Chemical Co., Niagara Falls, N. Y.

It is clear, from what Mr. Gregory has said about the conditions under which the electric generation of steam is commercially feasible that, in most instances, that application will be either one that takes place under unusual economic circumstances, or one that is a part-time application. In either case, of course, the apparatus must be relatively cheap, and this development of the electric boiler has brought it down to where it is extremely cheap.

The price for this particular form of apparatus runs, I understand, from about two dollars per kilowatt for the small sizes, up to something less than one dollar per kilowatt for large sizes, a price that, unfortunately, is rarely approached in other forms of electrical heating work.

However, though the apparatus itself is cheap, the subsidiary apparatus or other expenditures that may be necessary in installing this apparatus, can, unless the installation is laid out with a view to conditions, amount to many times the cost of the apparatus itself. This auxiliary apparatus may be in the form of transformers, wiring, switching equipment, etc., necessary to bring the power to the point of steam generation, or in the form of piping, etc., to take the steam to the point of consumption.

In most cases, these additional costs can be kept at a minimum by so arranging matters that you take advantage of the conditions which the particular problem offers of minimizing the expenditures that are necessary to bring the steam to the work, or the power to the work, as the case may be. It is for this reason that it is so important, as Mr. Gregory says, to consider every particular installation by itself. Any one who starts with the idea that he can go out and buy apparatus to take care of a certain amount of capacity, and leave the question of cost of installation till afterwards, as a minor matter, will be badly fooled.

In many cases, in plants that cover considerable areas, it would pay to install, instead of one large boiler, a considerable number of small boilers, just as it pays to put in a large number of small motors, instead of one large motor that requires a lot of transmission machinery. And this is made easy by the fact that these boilers require no control, or, at any rate, can be so run that all the control they require can be given by a man who goes around once every six or eight hours.

E. A. LOF[2]: The use of electric boilers on this continent is, as you know, comparatively new, although in Europe they have been used for a good many years. Hundreds of boilers are in daily use there, and I had occasion to see a good many of them a couple of years ago. It is remarkable, however, to note how quickly it is now being adopted here.

As one of the previous speakers brought out, electric boilers can only be used in connection with surplus power; that means power that is available during the night or over Sundays, and so on. During the day you usually have to rely upon coal-fired boilers, and that, of course, involves an investment for such boilers, in addition to the electric equipment.

Why not go one step further and do away entirely with the coal-fired steam boilers? This is entirely feasible, if, in connection with electric boilers, you install what are known as "steam accumulators" or "vapor accumulators"—large vessels filled with water—in which you can store the steam generated during the night and use it during the day. It is a proposition well worth looking into in connection with all electric boiler installations, especially large ones, such as those used by paper mills, etc. On my last trip to Europe, I was told that in Sweden they have installed over forty such installations during the past two or three years, and they claim that these installations pay for themselves in a couple of years' time.

CARL HERING[3]: I believe it was at the first meeting of this Society, twenty-one years ago, that I presented a little paper showing that when you electrolyze water under pressure the voltage diminishes, which seems to be paradoxical. There must be some electrolysis in these steam generators, because the current passes directly through the water between electrodes, and it seems to me that under the higher pressures in boilers, the voltage loss for electrolysis would then become less.

W. G. HARVEY[4]: The first question I would like to ask is, whether there is any electrolysis and therefore any evolution of gas in this apparatus? I assume that alternating current is used. The second question is, whether these machines can not be com-

[2] Elec. Engr., General Electric Co., Schenectady, N. Y.
[3] Consulting Elec. Engr., Philadelphia, Pa.
[4] Supt. and Met., American Magnesium Corp., Niagara Falls, N. Y.

bined with a regular coal-fired steam boiler so that the steam boiler could be heated during the day with coal and during the night with electricity when the cost of the current was low? It seems to me that if this could be accomplished, it would make an attractive selling proposition to plants of small size. Will the author give us an answer to these questions?

P. H. FALTER[5]: In regard to Dr. Hering's question about electrolysis, there is little known about the actual action of the current in these electric boilers, in regard to its effect in electrolyzing the water, or the formation of gas. But perhaps, talking from the standpoint of what is done to some of the parts of the boiler—and this isn't advertising—we have reason to expect that there is a certain amount of electrolysis. We do know that electrodes seem to wear entirely out of proportion to the input of energy. I mean that in boilers of certain designs you can put in a given amount of energy and get almost no wear on the electrodes; but in boilers of other designs you get a considerable wear for the same power input.

Of course, that may be assumed to be due to defective design, but that is not true. You proportion your gaps—what we call the gap, the distance from the electrode to neutral—in exactly the same way for different voltages, but you get different results. The electrode may wear rapidly, for instance, in the case of high voltages, and very slowly in the case of low voltages. That is perhaps negative. We do know from the textbooks, at least, or handbooks, that there is supposed to be a small amount of electrolysis even when using alternating current. Some authorities state that the amount is about one percent of what it would be with direct current, but another interesting thing comes in here and that is, that it varies greatly in these electric boilers, if we may attribute the results to electrolysis, with the frequency employed. At 60 cycles, I believe that it is inappreciable, but if you go down to 25 cycles, or even to 40 cycles, it makes a great difference.

You can take two boilers identically designed, one operated at 25 cycles, the other at 60, and your electrode wear will be decidedly different; it will be far greater in the case of the 25

[5] Vice-Pres. & Treas., Electric Furnace Construction Co., Philadelphia, Pa.

cycles than in the case of 60. I think that has some bearing on your question.

F. A. LIDBURY: Have you actually determined that?

P. H. FALTER: When you say "determined," I think of it quantitatively, and I would not want to say that we have determined it in a scientific way.

F. A. LIDBURY: I mean, did you try boilers at both frequencies?

P. H. FALTER: Yes, we had practically the same, identical design, the same water gap, and we found that difference.

The question is frequently asked if it is possible to make a combination coal-fired and electric boiler. Of course, it has been done, but by inserting the ordinary resistance element in the tubes or into the water of an ordinary boiler.

That always reminds me of the experience that certain people had in the city of Baltimore, when a few years ago gas became very cheap. On account of the peculiar situation in Baltimore, gas can be sold as low as thirty-five cents, and that suggested to people who wanted convenience, why should they not heat their houses with gas? They immediately consulted so-called furnace experts, who came forward at once with a few common burners and stuck them into the fire box of an ordinary furnace, with disastrous results. The gas bills were very high. The next thing that happened was that some more scientific fellow came along and designed a furnace to use gas. The gas bills for the users of such furnaces were decidedly lower, because the gas was applied efficiently.

I think the same is true in the case of these electric boilers. Why apply a device to a boiler designed for some other purpose? I mean, designed to operate in a certain other, decidedly different way. This electric boiler is a unit complete in itself, and, furthermore, it can be run in parallel with any other boilers, however fired. Another thing about it is, that it is so small as compared with any fuel-fired boilers, so clean, so simple in operation, requiring almost no attention, that I wonder why the suggestion is so frequently made that you should adapt a device to a piece of apparatus entirely different. Well, it isn't done—

that is the answer—and it is not difficult to convince a man in a few minutes why it shouldn't be done.

F. A. LIDBURY: The question of electrolysis is a rather interesting one. I have also had an opportunity of operating the same boiler with a 25-cycle current and a 60-cycle current, and the results I got bear out what we have just heard; the corrosion is less at the 60-cycle frequency. Unfortunately, in the case I am alluding to, the waters were different and conditions not being comparable, I could not draw the conclusion. In your case the water, I presume, was the same.

Of course, an easy way of determining what electrolysis does take place is to condense a certain amount of the steam and find out how much hydrogen is left. That would be an easy and direct way of measuring it, particularly as you would get a lot of hydrogen if a very small proportion of the current were producing an electrolytic effect.

However, apart from that, you must not assume that, because you get corrosion in these boilers, it is electrolytic in the sense that it is determined by the current that is passing through them. One peculiarity of this type of boiler is, that you can have, within the space of a foot or so, the water at very different degrees of concentration and of temperature. Under those circumstances, if, without passing any current through them at all, you could maintain them in that condition for a considerable length of time, you would probably get a great deal of corrosion.

P. H. FALTER: That is a question that is often asked by critical people, whether we produce hydrogen, and if so, how much, and is there a danger of explosion. If the facts that have been observed can be considered as having been caused by electrolysis, the answer is that there is no danger, because the amount of electrolysis is so small that the amount of hydrogen formed is not sufficient to cause an explosion, even if it could stay in the boiler. But how it can stay in the boiler with steam flowing I do not know.

P. S. GREGORY: Mr. Lidbury mentioned an important point when he said that the cost of the electric generator was not the greatest factor in the cost of the installation. For instance, in two large units, one at Shawinigan Falls and the other at Grand

Mere, the cost of the steam generator was only about 25 per-cent of the total cost of the installation, because in both cases the cost of the power line was high and a considerable amount of steam piping had to be done.

P. H. FALTER: I would like to touch on the cost of these things. It is commonly assumed that they are very cheap, and they are when they are large, but they are not so cheap when they are small, yet the boiler itself is cheap. But when you get a small unit, the electrical equipment required with it costs more than the boiler.

There is another feature; you can not build these boilers in units or standards, because they are not applicable in may places. In the first place, we heat water either to the temperature of steam, or below. There are two conditions. Then we are required to design the apparatus for atmospheric pressure, low pressure steam and high pressure steam. There are three distinct conditions. Then, finally, we have voltage, and all of you know what the range of voltage is. In the boilers that are now in use it actually ranges from 110 to 12,000 volts, and there are a great many stopping places in between. Any mathematician can easily figure out the permutations and combinations.

ACHESON SMITH[6]: I would like to suggest one instance of the applicability of this boiler that I have not heard mentioned; that is the possibility of using it for balancing phases. There are many furnaces that use either single-phase or two-phase current, and the difficulty is with the third. It occurred to me that a boiler might be run on a single phase. The power companies are becoming more and more insistent that the three phases be balanced.

P. H. FALTER: The simplest form of boiler is the single-phase boiler. The ordinary boilers with small capacities have three phases and one tank. The larger sizes are all single-phase boilers.

[6] Vice-Pres. and Gen. Mgr., Acheson Graphite Co., Niagara Falls, N. Y.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 22, 1922, Vice-President Crosby in the Chair.

A NEW INDUCTION FURNACE.[1]

By J. Murray Weed.[2]

Abstract.

In this new induction furnace for melting non-ferrous metals the secondary consists of a molten charge which is distinct from the melting pot. There is, however, automatic uni-directional circulation produced between them by the force of electromagnetic repulsion. It is shown that the maximum and minimum fluid pressures in the secondary exist at the ends of the cylinder, which pressure difference is utilized in causing the molten metal, of high or low conductivity, to circulate. [A. D. S.]

It is the object of this paper to describe a new induction furnace for melting non-ferrous metals, possessing some features which differ radically from those found in any previous furnace, and affording great flexibility of design, and a broad scope of application.

In this furnace, as in other induction furnaces, the heat is produced by an electric current induced by transformer action in a looped portion of the molten charge, which we call the secondary. This secondary is distinct from the melting chamber, or pot in which the cold charge is received, melted and held for refining and pouring. The success of the furnace depends upon a continuous, automatic circulation of the molten metal between the secondary and the melting pot, to prevent overheating in the former and to deliver the heat to the cold metal in the latter. It is in the form of the secondary, and in the character of the circulation and the method of producing it, that the new fundamental features of this furnace are found.

[1] Manuscript received August 7, 1922.

[2] Power and Mining Engineering Dept., General Electric Co., Schenectady, N. Y.

The secondary loop in this furnace closes upon itself without passing through the melting chamber, as illustrated by sectional views in Fig. 1. It is in the form of a hollow cylinder, of considerable length, which communicates with the melting chamber through two distinct ports or passages, from opposite ends of the cylinder. The current flows around the cylinder in a cir-

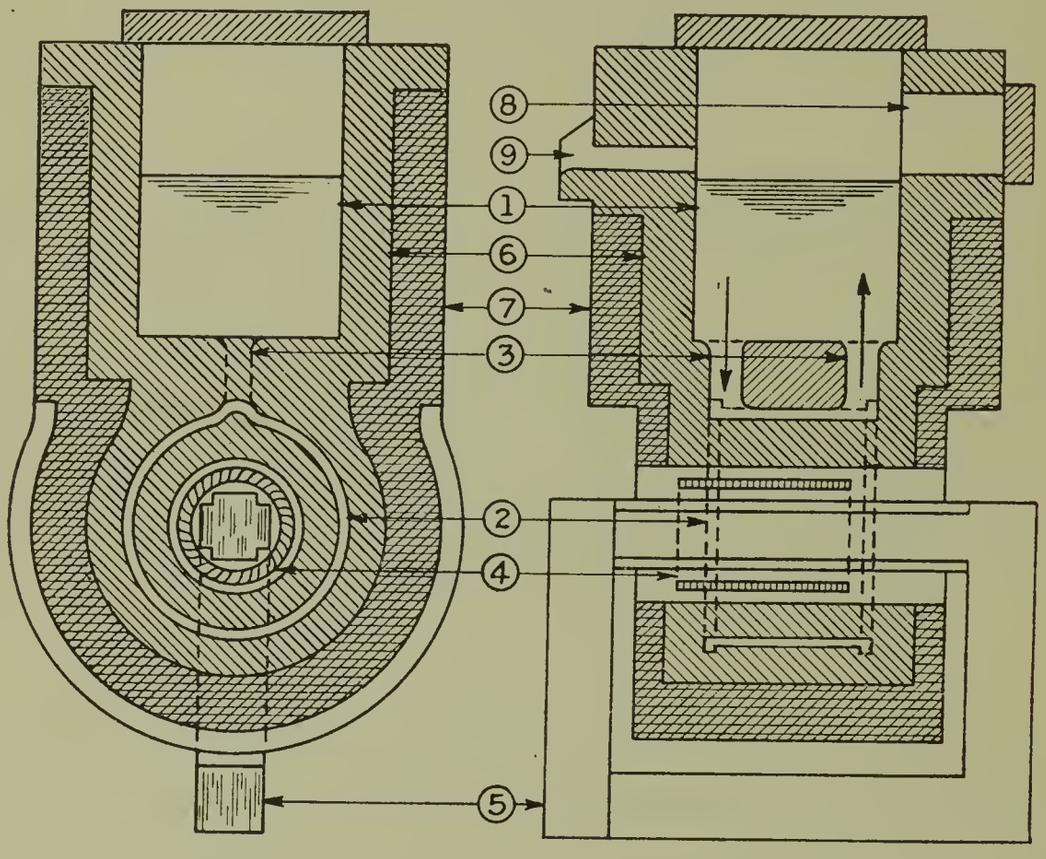


FIG. 1

Two vertical sections of the furnace at right angles to each other. 1. Molten metal bath in melting chamber; 2. Molten metal secondary cylinder in which heat is generated by induced currents; 3. Ducts for uni-directional circulation of the metal; 4. Primary Winding; 5. Laminated iron core; 6. Refractory lining; 7. Thermal insulation; 8. Charging door; 9. Pouring spout.

Note the thickened sections at the ends of the secondary cylinder, one serving as a channel for distributing the metal around the perimeter of the cylinder and the other for collecting it. The flow within the main body of the cylinder is in an axial direction.

Note the axial displacement of the primary winding with respect to the secondary. The velocity of the circulation of the metal may be varied by shifting the position of this winding.

cumferential direction without entering the chamber or communicating passages, while the circulating charge flows through it in an axial direction, transverse to the current. The movement of the molten metal is uni-directional, from the secondary cylinder to the melting chamber by one passage and from that chamber back to the secondary by the other.

The circulation in this furnace is effected by the force of electromagnetic repulsion, set up through the medium of the magnetic leakage field, which exists between primary and secondary in any transformer. This force is proportional to the square of the current flowing, and is familiar to all transformer engineers as having caused much trouble in the wrecking of transformers when the windings were not held with sufficient rigidity to withstand the enormous forces of this nature which are set up when short circuits occur.

The induction furnace is, in fact, a special case of a short circuited transformer, in which the internal impedance is comparable with the total full load impedance of the secondary circuit of the ordinary transformer. The repulsive force in this furnace, therefore, is not excessive, as in ordinary transformers when short circuited, but only such as exists in ordinary transformers when normally loaded.

Some explanation may assist in understanding how this repulsive force becomes effective in producing circulation of the molten material through the secondary, while the secondary itself is fixed in position.

In the case of an ordinary transformer, with solid secondary, relative motion between primary and secondary occurs only when the strength of the structure supporting the windings is not sufficient to withstand the force corresponding to the current flowing, and when such motion does occur, the current and its conducting medium, the solid metal of the coil, necessarily move together. In this furnace the case is quite different. The repulsive force will always be small, relative to the physical strength of the structure as a whole, and while the secondary current and the position of the secondary do not shift, yet the secondary conducting medium can and does flow. This difference is understood after considering the nature of the magnetic leakage field, which is the same in both cases, and the natural effect of the modified conditions upon its action.

The physical characteristics by which any magnetic field makes itself apparent are those of mechanical attraction and repulsion, and of inducing voltages in conducting media when relative motion not parallel to the field occurs between it and the conducting medium. A force of attraction exists between unlike mag-

netic poles, while a force of repulsion exists between like poles. The former force is due to a tractive effort or tensile stress exerted by the field in directions parallel to itself, while the latter is due to a pushing effort or compressive stress in a direction at right

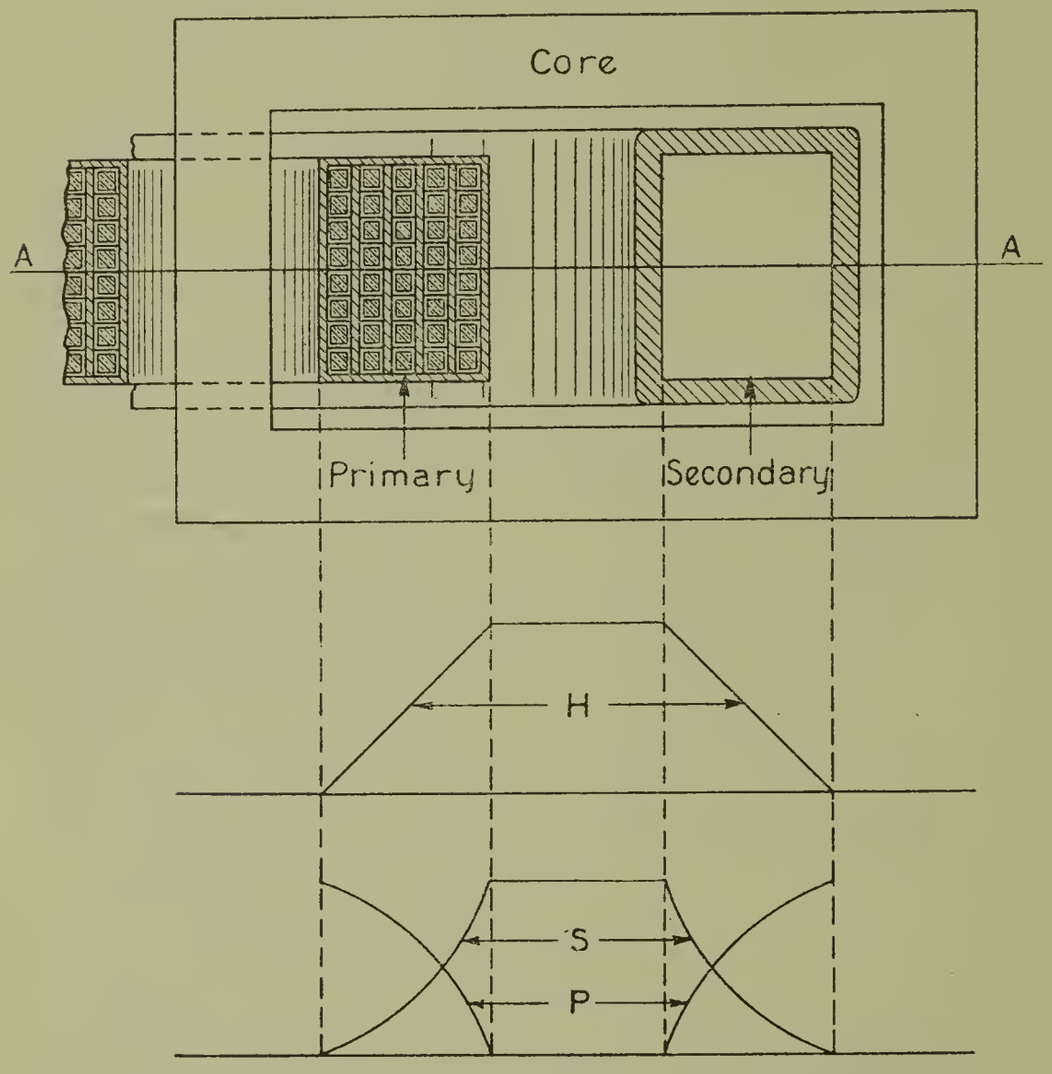


FIG. 2.

Transverse section through primary and secondary of a hypothetical furnace, with curves.

H shows the variation of the density of the magnetic leakage field between primary and secondary along lines parallel to A-A.

S shows the variation of the stress in the field which is proportional at every point to the square of the density.

P shows the variation of the fluid pressure in the molten metal. The difference between the fluid pressures at two points is equal to the difference between the corresponding stresses of the field. The maximum fluid pressure occurs in the part of the secondary most distant from the primary where the minimum stress is found.

angles to the field. These stresses are true mechanical stresses, measurable in grams per sq. cm. or pounds per sq. in., which exist simultaneously in any magnetic field, and which produce the results which such stresses would be expected to produce.

The stress involved here is that of pressure at right angles to

the field, this field being the leakage field between primary and secondary. In the case of the solid secondary of the ordinary transformer, if it is free to move, bodily motion will be produced. If it is properly supported, although mechanical pressure is produced, no movement occurs. In the case of the fluid secondary of the furnace, the mechanical pressure appears as a fluid pressure and even though the secondary as a whole is not free to move, this fluid pressure, if not uniform, and if permitted to do so, will cause the metal to flow from points of higher pressure to points of lower pressure. It remains now to show that the pressure is greater at certain points in the secondary than at certain others, and to show how this pressure difference is utilized to produce the desired circulation.

The leakage flux between primary and secondary is not all confined between their adjacent boundaries. This matter has been carefully investigated for transformers, and for an arrangement with transverse cross section such as is illustrated in Fig. 2, for instance, the distribution of the leakage field is shown by the curve H, the ordinates representing the magnetic densities at points along lines parallel to A-A. In both primary and secondary, the density falls away gradually, from its maximum value at adjacent boundaries, and disappears at the further boundaries. As the stress in the field at any point is proportional to the square of the density, the variation of the stress along the line A-A is in accordance with the curve S. This, however, does not signify that the mechanical or fluid pressure imparted to the secondary (or primary) is represented at each point by the ordinate of curve S.

Were the density of the field uniform throughout, the magnetic stress at any point would be counter-balanced by equal stresses at all other points, and no mechanical pressure would be imparted to the material medium. It is only the difference between the magnetic stresses at given points in the secondary that appears between those points as mechanical pressure.

If the differentials of pressure be added along the line A-A, from the side of the secondary nearest to the primary to the side farthest from it, the integrated or effective pressure will be represented by curve P, such that the ordinate of P at any point added to the ordinate of S equals the maximum value of S. The ordinate of curve P at any point represents a pressure difference between

that point and a point at the side of the secondary nearest to the primary.

In the case of the fluid secondary found in the furnace, this pressure difference constitutes a difference of fluid pressure. It cannot equalize itself within the secondary, since it is opposed by the stresses of the field which sets it up. If, however, a passage or passages be provided external to the secondary, from the point of maximum pressure (farthest from the primary) to the

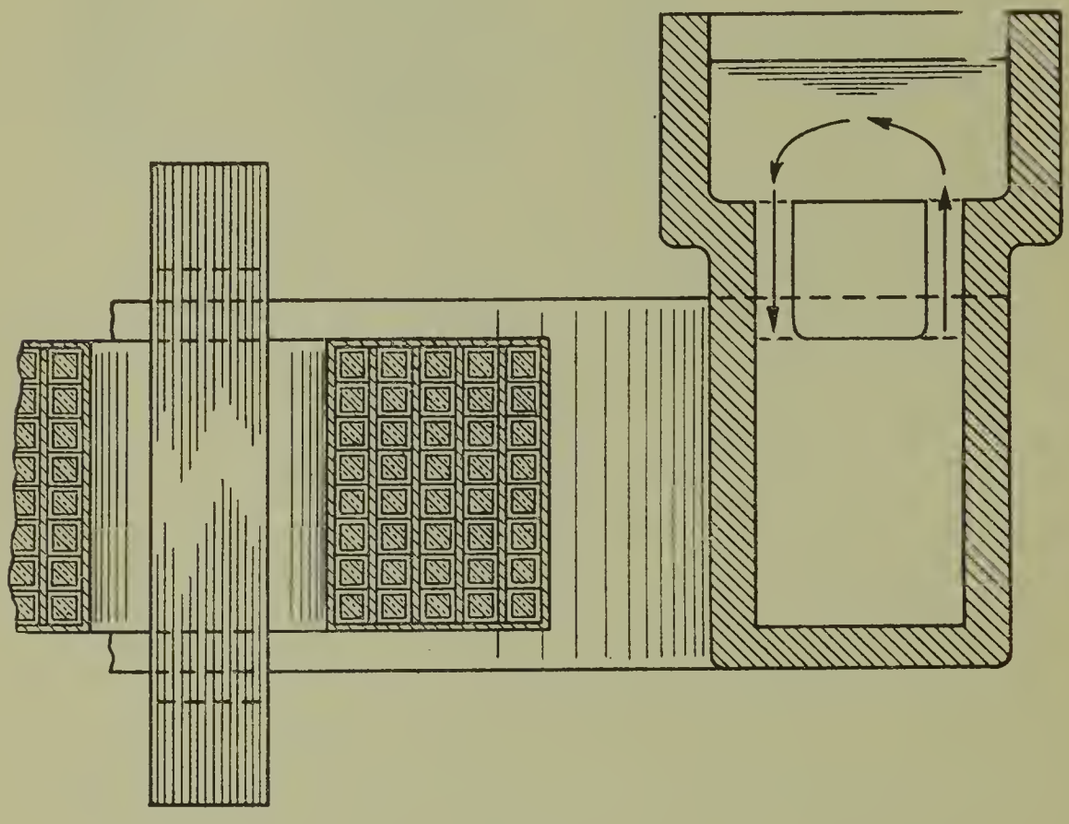


FIG. 3

Section of hypothetical funace shown in Fig. 2, perpendicular to the section in that figure. The arrows show the way molten metal would flow through the external channel and reservoir, from the point of higher fluid pressure in the secondary to the point of lower fluid pressure.

point of minimum pressure, (closest to the primary), as illustrated in Fig. 3, the pressure difference will cause the fluid to flow, as indicated by the arrows.

The pressure causing this flow will be maintained by the field, with a corresponding internal flow from the point of minimum pressure to the point of maximum pressure. The strength of flow will be such that the sum of the internal and external pressure drops due to friction will be equal to the total pressure imparted or generated by the field.

Figures 2 and 3 have been used here for the purpose of illustrating, in the simplest manner, the principle involved. The arrangement of primary and secondary in the furnace, as actually developed and represented in Fig. 1, differs from that in Figures 2 and 3 for practical reasons, but the principle is the same. Maximum and minimum fluid pressures are found at the ends of the secondary cylinder which are respectively farthest from and nearest to the primary winding as a whole, or to use a form of expression common with transformer designing engineers but somewhat lacking in definition, at the ends which are farthest from and nearest to the magnetic center of the primary winding. This pressure distribution results from the diagonal arrangement of the leakage field, due to the axial displacement between the primary and secondary. It is the radial component of this field which generates the pressure difference between the two ends of the cylinder.

That the axial forces set up in such an arrangement are substantial realities, has been demonstrated by experience in transformers with windings of the concentric cylindrical type. Comparatively small axial displacements of these windings have, upon numerous occasions, resulted in crushing the mechanical supports of the coils and deforming the coils themselves, the primary being driven in one direction against the yoke of the core, and the secondary in the other. The differences in fluid pressure between the two ends of the secondary cylinder in the furnace are demonstrated by the flow of the molten metal in the furnace. Any reasonable velocity of the circulation can be easily obtained, by merely adjusting the axial position of the primary winding with respect to the secondary, for which provision is made in the mechanical design of the furnace.

As intimated at the beginning of this paper, the chief significance of the new physical features which have been described above lies in their effects upon flexibility of design and scope of application. The free uni-directional circulation, set up by a force which can be controlled within desirable limits, not only restricts the temperature variation of the metal to a small value, but also avoids the danger of magnetic choking.

This makes it practicable to force the furnace to any extent which is feasible for the primary winding and core, and particu-

larly adapts it for the melting of high conductivity metals, such as copper, as well as of metals of lower conductivity. The form of the secondary is favorable to flexibility of design as regards size and capacity. The only limiting feature in this direction consists in the refractory lining, due to considerations of mechanical strength and general reliability. Such limits are probably capable of indefinite expansion. Increased size and capacity will have no necessary effect upon the power factor, which is inherently high with the long thin section of the secondary.

DISCUSSION.

Oscar Brophy[1] (*Communicated*): On first reading this paper one gets the impression that the circulation of the molten metal in this furnace is dependent upon the magnetic leakage field between the primary and secondary of the transformer. Magnetic leakage in a transformer is the term used to describe that part of the magnetic field that encircles one coil only. In well designed transformers this leakage field is practically eliminated, as is shown by the high power factor obtained. This is accomplished by placing the primary and secondary coils as close together as possible. When the leakage field is eliminated does this electrodynamic force disappear? No, instead, this force increases, for we know that the repulsion between two conductors carrying currents in opposite directions is inversely proportional to the square of the distance between them.

Take the case of "pinch effect" in a molten conductor. Here we have a single conductor carrying current, and no such condition as leakage field, yet the electrodynamic force of attraction manifests itself forcibly. Also, in the case of a molten conductor which takes the form of an acute angle, the electrodynamic force of repulsion manifests itself. Here again there is no such condition as leakage field. It is simply a case of two conductors carrying currents in opposite directions. Therefore, the statement that an electrodynamic force is set up through the medium of a leakage field is misleading. The term "magnetic leakage field" in a

[1] Philadelphia, Pa.

transformer is used to explain the less than unity power factor of the transformer, and certainly has no connection whatever with electrodynamic forces.

These electrodynamic forces are set up between conductors carrying currents, and if one of these conductors is a fluid it will flow and the direction of the flow will depend on the relative position of the two conductors, and the direction of the current. Let us assume that in this furnace there is no axial displacement of the primary, as shown in Fig. 4. Consider a point P at the middle of the primary and a point S at the middle of the secondary. The force between them will be in the direction as shown by the arrow, that is, a radial direction, and will have no component in the axial

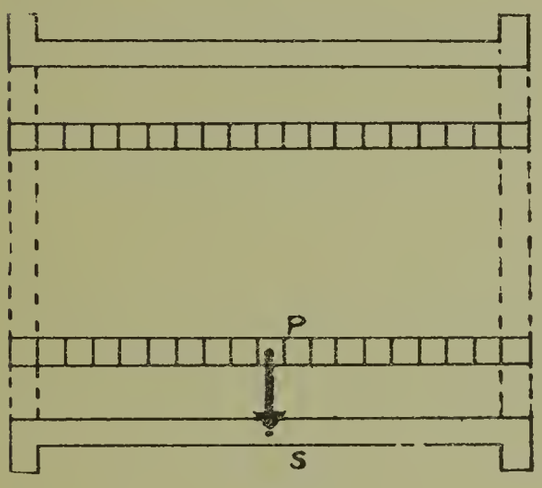


FIG. 4

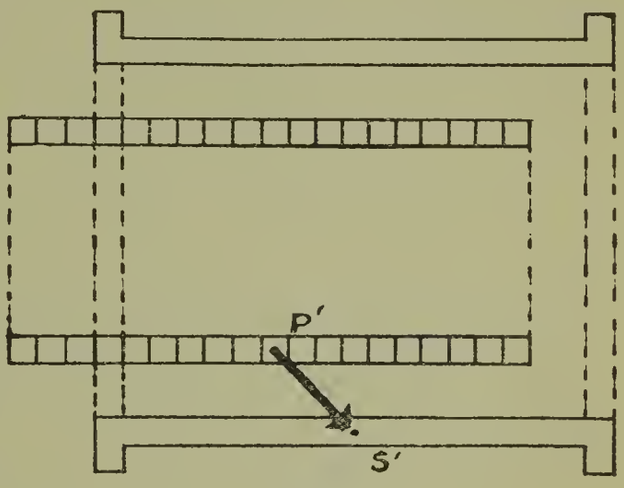


FIG. 5.

direction, and therefore there will be no flow in the axial direction, only a churning up of the metal in the secondary and no flow of metal up into the bath.

Now consider Fig. 5, in which there is an axial displacement of the primary. The direction of the force between the two center points P' and S' will be as shown by the arrow, which has a component in the axial direction, and hence the metal will flow in this direction and therefore up into the bath.

In a constant current transformer this force of repulsion is used. The primary and secondary coils are co-axial and placed one above the other. If the two coils were concentric, that is, no axial displacement of the coils, there would be no movement, because the force exerted between the two coils would be in a radial direction and balanced. It is only when you displace the coils axially that you get a movement in an axial direction.

The flow of metal in this furnace depends upon two facts—

1. There is an electrodynamic force of repulsion between the primary and secondary, as their currents are in opposite directions.

2. This force is given an axial direction, so as to cause the metal to flow up into the bath by means of the axial displacement of the primary.

The method of producing this circulation is not new, as it was first described by the writer in U. S. Patent 1,296,752, granted March 11, 1919.

CARL HERING[2]: I am very much interested to see that these electromagnetic forces are coming into use in electric furnaces, as I have fathered them for many years; they are so easily produced and they are so serviceable. If the circulation produced by these forces is in an upward direction, there is probably nothing that will act better to cleanse metals than such a circulation. It brings every part of the metal in turn to the top; all the suspended impurities are thereby brought to the top, and when they get there they stay there. I have watched this myself, and have seen the molten particles brought up by these forces, and when they reach the top they spread out like a drop of oil will, and then they stay there.

There are several hundred furnaces in daily use in which these electrodynamic forces are being used, and the reason is chiefly that the metals are cleansed and made homogeneous.

I do not agree with the author in his explanation. It seems to me his explanation is unnecessarily involved. Some thirty or more years ago, Elihu Thomson showed that if you put a copper ring over an alternating current magnet that it is repelled, it is pushed off. It seems to me that this is all that is necessary to explain this furnace. It is not necessary to go into all the detailed explanations that Mr. Weed has given here to show the action of that force. Why give such an involved explanation?

Magnetic attractions and repulsions are physically exactly the same phenomena, except that the sign is changed. When there is attraction between two conductors, the flux goes around both, and there is absolutely no leakage flux. Therefore, why drag in the leakage flux as the crucial element?

[2] Consulting Electrical Engr., Philadelphia, Pa.

The explanation that the force is due to the leakage flux is, in my opinion, not quite rational; at least, it is not the best explanation. Moreover, the author contradicts himself when he says that the leakage flux causes this motion, and then says that the leakage flux is low, because the power factor is high. If the leakage flux were the cause of all this motion, it ought to be made great so as to cause a greater motion, and that would lower the power factor.

At the bottom of page 238 he says, in effect, that the energy of the flow is used up entirely in friction. I do not agree with him in this. I have worked much with furnaces of this general type, and in one case the energy set free mechanically in the liquid was about 50 percent of the total, about 50 kilowatts out of 100. It seems to me the greater part of the mechanical energy that is put into this circulation is due to the fact that a lot of heavy metal is being put into rapid motion. Therefore, it is inertia rather than friction.

In my opinion, the mechanical energy in this general type of furnace had better be made as great as possible, not as small as possible. The more mechanical energy there is set free in this type of furnace, the better, because the electrical conditions will be more favorable. Such energy is not lost, as it all goes into heat in the friction of churning the metal; this churning can be made quite violent.

The author speaks of the limitations. It seems to me the induction furnace has very grave limitations. It has two holes through the refractory material, one hole for the core and another one for the metal. These two holes, involving a rather thin lining, it seems to me, constitute the chief limitation of this furnace. The linings must necessarily be thin or the power factor will become low. The bending strains on those thin linings are rather great; the failures of induction furnaces of this general type in the past have been largely due to the thinness of the lining, which is necessary in such an induction furnace.

On the other hand, the uni-directional flow—that is, having the flow always in one direction—is a great advantage. In other induction furnaces of this general type that are in extended use the flow is bi-directional; it is in and out. With a uni-directional flow, the furnace can be forced.

J. A. SEEDE[3]: I think this occasion should not be allowed to pass without emphasizing the value of Mr. Weed's work. He has, by an ingenious arrangement, made use of forces that all transformer designers know of, and produced a furnace which for the first time to my knowledge makes the metal flow continuously in one direction. Now the metal can be made to flow quietly, which to me is desirable, or violently, as may be necessary, as pointed out by Dr. Hering. Of course, if it is made to flow violently it might wash out the lining and cause trouble in that way.

Also, I believe this furnace is the first one that has ever made use of a pre-formed lining, largely due to the work of Mr. Unger, and also it is the first furnace of the induction type that will successfully melt copper, aluminum and other high conductivity metals.

J. RATTRAY WILSON[4]: I would like to ask Mr. Weed if the velocity of circulation through the various parts, the cylindrical secondary and the ports, is the same; that is, is equilibrium maintained to get the same velocity through?

J. MURRAY WEED: Referring to Mr. Brophy's discussion, he criticized my attributing this circulation to the magnetic leakage, and says it is due to the repulsion between primary and secondary. It is this magnetic leakage field which produces repulsion between primary and secondary.

Mr. Brophy spoke of a furnace on which he took out a patent some years ago, in which this force was used. I am familiar with that patent of Mr. Brophy's; he has not used the force because he has not provided any passage for the metal to return to the secondary at the other end of the cylinder. He has only provided passages from the secondary to the pool at one end. You must have a return passage for the molten metal to get circulation.

It was suggested that I should have given a bibliography, calling attention to previous furnaces of this type. The new furnace described in this paper is the only furnace that I know of in which the secondary and primary have been so constructed and so arranged with respect to each other as to give the repulsion between them an opportunity to produce a distinct unidirectional circulation.

[3] General Electric Co., Schenectady, N. Y.
[4] Elec. Engr., Electric Smelting Co., Hull, P. Q., Canada.

Dr. Hering's criticism of the leakage field was along the line of Mr. Brophy's. I think the same answer will apply; it is the leakage field that produces the repulsion between primary and secondary.

CARL HERING: There is no leakage field when there is attraction, and attraction and repulsion are simply different in sign.

J. MURRAY WEED: There is a fundamental point on which I would differ from Dr. Hering. Attraction is due to the shortening of lines of force in a magnetic field, while repulsion is due to the tendency of the lines to separate from each other. We get the former between unlike poles; we get the latter between like poles.

J. RATTRAY WILSON: My question was with reference to the cross-section.

J. MURRAY WEED: The section at the ports or channels—where the metal flows from the secondary out into the reservoir and back—is smaller than the section in the secondary itself, because we have a complete cylinder of that metal, and the metal is flowing in an axial direction.

W. G. HARVEY[5]: In describing his apparatus, Mr. Weed mentioned that the circulation of the charge was aided, or the return flow to the secondary was assisted, by the atmospheric pressure on the body of the charge. I should think that this pressure would be neutralized, inasmuch as it is also effective on the upflow portion. There could, therefore, be no force causing the flow except the electrical.

J. MURRAY WEED: So far as circulation is concerned, the atmospheric pressure and the head of the metal are acting upon the upward flow, as well as the return flow. But the point I was trying to make is this: Suppose we block up the return channel altogether; then, in order to force the metal out, we would have to overcome the head of the metal, plus the atmospheric pressure, leaving a vacuum in the cylinder. But if the channel is not closed, we have the head of the metal and the atmospheric pressure to force molten metal in through this channel and fill this vacuum, and you can see at once that metal would flow in very

[5] Supt., American Magnesium Corp., Niagara Falls, N. Y.

rapidly, before you could get a vacuum. That is why we cannot get magnetic choking. What I mean by magnetic choking is a reduction of the cross-section of the secondary metal.

J. MURRAY WEED (*Communicated*): I feel that the doubts raised by Mr. Oscar Brophy and Dr. Carl Hering regarding the soundness of my explanation of the circulation in this furnace were not adequately answered in my oral discussion.

As to the dependence of the repulsion between primary and secondary in any transformer upon the magnetic leakage field—the furnace is a special kind of transformer—I refer Mr. Brophy and Dr. Hering to a paper on "Mechanical Forces in Magnetic Fields" by Dr. C. P. Steinmetz, published in Volume XXX of the Transactions of the A. I. E. E. A section of the paper relating to "Short Circuit Stresses in Transformers" begins on page 377. Detailed methods of calculating these stresses, based upon the density of the magnetic leakage field, are given in my discussion of that paper beginning on page 399 of the same volume.

That attraction between conductors carrying currents in the same direction is due to tension in the magnetic field, or lines, which surround them both, and that repulsion between similar conductors carrying currents in opposite directions is due to pressure or mutual repulsion between the lines passing between them, are taught in the standard text books on physics. The conditions for repulsion hold equally whether the conductors considered are parts of the same continuous conductor which has been bent back upon itself with the same current flowing through both parts in series, as in the case of the molten conductor with the acute angle referred to by Mr. Brophy, or whether they are entirely separate and carry distinct currents, as in the primary and secondary windings of transformers. In this latter case the intervening field is the leakage field.

That the co-existence of high power factor and large mechanical forces is not inconsistent with their mutual dependence upon magnetic leakage, as contended by Mr. Brophy and Dr. Hering, is seen when it is considered that the reaction voltage, which affects the power factor, is proportional to the product of the leakage flux by the number of turns, while the mechanical stress is pro-

portional to the square of the flux density. If the windings of a transformer are close together, the density of the leakage flux may be very high, and yet its total amount relatively small.

To say that a copper ring is "repelled" or "pushed off" does not explain that fact, nor does the statement that "electro-dynamic forces are set up between conductors carrying currents" explain itself. These phenomena can be explained only by a consideration of the field existing between the elements which repell each other. Further considerations than this, however, are involved in the explanation of the circulation of the molten metal in the furnace. The field existing between the primary and the secondary as a whole, in this case, has no effect, since the secondary as a whole is not free to move. The explanation depends entirely upon variations in the density of those portions of the leakage field which exist within the boundaries of the secondary, linking a portion of the secondary and leaking from another portion. These density variations result in variations in the fluid pressure, thus producing the circulation as explained in the paper. I hope that Dr. Hering will see that the explanation given is rational and not unduly complicated.

Dr. Hering stated that he did not agree with me that the energy of the circulation is used up in friction, and yet, in the next paragraph, he says that "such energy is not lost, as it all goes into heat in the friction of churning the metal." I agree fully with Dr. Hering's latter statement.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 22, 1922, President Schlueder-berg in the Chair.

A SIMPLE ELECTRIC CRUCIBLE FURNACE FOR MELTING ALUMINIUM.[1]

By A. Glynne Lobley[2]

Abstract.

A small electric resistance furnace of a capacity of 60 kilos of brass is described. The heating element consists of nichrome ribbon. [C. G. F.]

It is generally recognized that in certain high temperature processes, and in cases where rapidity of melting is a criterion, the electric furnace may advantageously be used. But it is not equally realized in England that electric heating may economically replace fuel furnaces for processes of the opposite type, such as slow melting at low temperatures and the maintaining of metals molten over long periods.

It is the purpose of this paper to describe a case in which electricity was applied to the melting and keeping molten of aluminium for die-casting small objects. Such an instance is one which at first sight would hardly be thought to afford an economical opportunity for electric heating, in view of the simplicity with which gas may be used for that purpose. Nevertheless, an economical superiority does exist, due, primarily, to the greater facility with which the electric furnace may be thermally insulated.

The problem before the writer was to design an electric crucible furnace which would be equally convenient in operation, inexpensive to erect, and even with the small output of 85 to 100 lb. (38.6 to 45.4 kg.) per crucible per day, no more expensive in running costs than the gas furnace it was intended to supplant.

The arrangement adopted is shown in section in Fig. 1. It consists essentially of a nichrome ribbon resistor, wound in a helix and supported on thin firebrick shelves round the crucible but not touching it. The crucible is removable for renewals without disturbing the resistor, and the whole is heat insulated with kiesel-

[1] Slightly abridged, manuscript received August 22, 1922.

[2] Reader in Electrochemistry, the Victoria University of Manchester, England.

guhr and special bricks, held in a container of ordinary brickwork. The helical arrangement made it possible to have sufficient area of resistor for the heat to be radiated and convected from it with a comparatively small difference of temperature between it and the crucible. Part of the resistor is carried under the crucible.

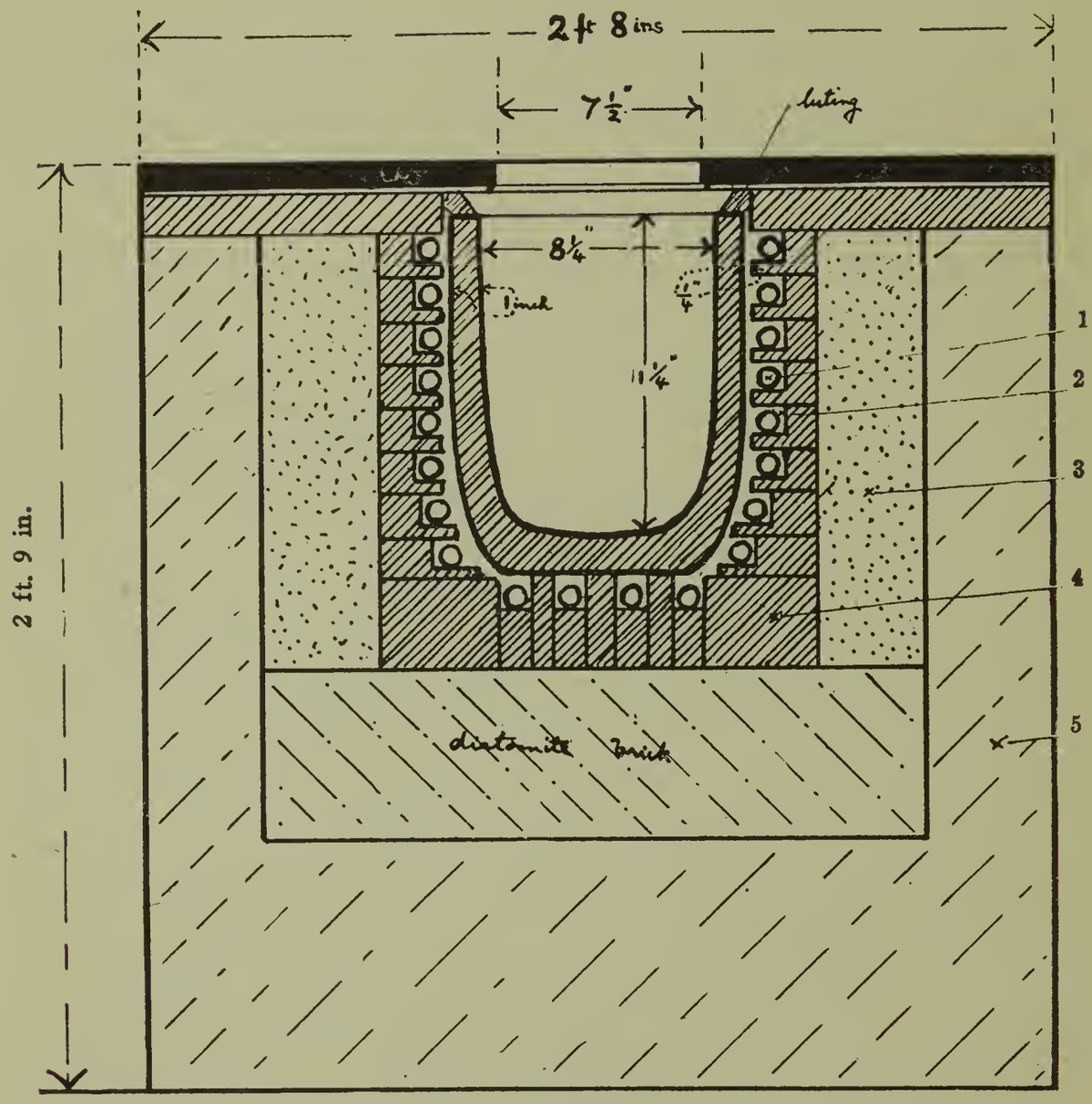


Fig. 1. Section of Furnace. 1. Resistor. 2. Shelves. 3. Kieselguhr. 4. Firebrick. 5. Ordinary brick.

When first started, a plumbago crucible was used, but after running for some weeks the graphite was burnt out of the outer layers, leaving a porous clay mass of poor heat conductivity, with a consequent falling off in the efficiency of the furnace. A plain fireclay crucible was then substituted for the plumbago one, and this gave much better results.

DETAILS OF FURNACE.

Crucible: Morgan's (Battersea, London) shape A, size 60. Capacity, 60 kilos of brass, *i. e.*, 35 to 40 pounds of aluminium.

Resistor: Nichrome II ribbon 0.25 by 0.04 in. (6.3 x 1 mm.), wound in a helix 0.875 in. (22 mm.); external diameter, from 2.5 (at bottom) to 1.8 (at top) turns per inch; length of ribbon, approximately 155 feet (47.2 m.); length of helix, 27 feet (8.2 m.); resistance when hot, 10 ohms.

Voltage on furnace terminals: full on, 200; approximately half on, 135; approximately third on, 112.

Current varies slightly with temperature of furnace, owing to difference in resistance of ribbon, but is approximately 20, 13.6, and 11.4 amperes for above voltages. Kilovolt-amperes corresponding to above, 4.0, 1.8 and 1.3.

Exposed surface of ribbon: 3.75 sq. ft. (0.35 sq. m.) while the outer surface of crucible was 3 sq. ft. (0.28 sq. m.) On full power, 7.4 watts per sq. in. of exposed resistor surface, the exposed resistor surface being taken as area of one side and two edges of ribbon.

External diameter of special firebrick cylinder: 15.5 in. (39 cm.); average thickness of kieselguhr insulation, 5 in. (12.7 cm.). Insulation brick, in vertical planes, replaces the kieselguhr at intervals, to give the necessary mechanical support to the internal structure.

The resistor was sprung into position and showed no tendency to touch the crucible. It could, however, easily have been fastened in place if desired. The crucible was luted round the top edge (as shown), the iron plate being afterwards placed in position. While metal was being ladled the top was covered with a canopy open on one side, to minimize the heat losses; and when not ladling with an insulated flat cover.

In this work an aluminium alloy containing 8 percent of copper was being used, and in an average week 465 lb. (211 kg.) were melted with an energy consumption of 362 Kw. H.; that is 4 Kw. for 37 hours 1.8 Kw. for 87 hours, 1.3 Kw. for 44 hours. Kilowatt hours per pound of metal melted, 0.78.

The crucibles cost two-thirds of the plumbago ones used in the gas furnace, and the life was at least as long, the minimum being two months. The cost of power and crucibles (Sheffield

prices in 1920) was 1.07 pence per pound, while with the gas furnace the cost was 1.26 pence per pound.[3] The furnace gave no trouble and was much superior in every way to the gas furnace.

There was no opportunity of getting reliable figures of the metal losses, but they were quite evidently less, and the metal appeared much cleaner than with the gas furnace.

The writer admits that the simple experimental furnace described has only a low thermal efficiency, but that is inevitable where the ratio of output to capacity is so small, and where a crucible, open a large part of the time, is used; but he hopes to have shown that even under these conditions the electric furnace can successfully compete with the fuel furnace.

Unfortunately, in Great Britain the preference shown by many foundrymen for crucible melting has played a large part in hindering the adoption of electric furnaces in non-ferrous work, and even at the present time they are little used.

In dealing with larger masses of aluminium the writer has designed and used granular carbon radiation furnaces; and as far back as 1918 had a large rectangular tilting furnace with a capacity of 1,500 pounds of aluminium, in successful operation. The design was on the same principle as the Baily furnace, but was independently, and apparently simultaneously, arrived at. It was the result of a series of experiments which showed that neither the induction nor the arc types was as suitable for aluminium as the radiation resistance.

As in the furnace described by D. D. Miller[4], there were two troughs containing the granular carbon, but the electrodes, trough supports, and mechanical arrangements were different. This furnace was probably the first non-ferrous electric melting furnace in Great Britain, but at this date a description of it would not be of interest, as a similar furnace, the Baily, is well known; moreover, it would be outside the scope of this paper.

The present crucible furnace was erected for The Sheffield Flatware Company, Ltd., and the writer desires to record his thanks to Dr. R. S. Hutton and The Sheffield Flatware Company for permitting this account of it.

[3] At 1.3 pence per Kw. H., and 47 pence per 1000 cu. ft. of gas.
[4] Chem. and Met. Eng., 1918, 19, 251.

Electrochemical Laboratory,
Victoria University of Manchester, England.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 22, 1922, President Schlueder-berg in the Chair.

MANUFACTURE OF CARBON BISULPHIDE.[1]

By Geo. A. Richter[2]

Abstract.

A new plant for the manufacture of carbon bisulphide is described. The furnace consists of a refractory lined cast iron shell. A resistance bed of broken arc light carbon is distributed between the electrodes. Charcoal and liquid sulphur are periodically fed into the furnace. Detailed thermal data are submitted, indicating that the process is operating comparatively efficiently.

[C. G. F.]

In the past twenty years there have appeared from time to time in various technical journals, articles describing in some detail the manufacture of carbon bisulphide in the electric furnace. Most of the articles in recent years have referred specifically to the so-called Taylor process. By using production data and power-consumption figures given by Mr. Taylor, others have calculated the approximate thermal efficiency of the operation. Such estimates are based upon the thermal constants to be found in the literature, and indicate a thermal efficiency ranging from 35 to 55 percent, according to the assumptions made.

It has been thought of sufficient interest to go into the study somewhat further, with a hope of striking a thermal balance in order to approximate at least the distribution of heat losses in the manufacture of carbon bisulphide.

Inasmuch as the writer has had no personal experience with the Taylor method of making carbon bisulphide, it will be necessary to make such calculations from data obtained from a manufacturing process which differs in some essentials from the better-

[1] Manuscript received August 28, 1922.

[2] Research Department, Brown Co., Berlin, N. H.

known Taylor process. In order to avoid a misunderstanding, it will be advisable (1) to review the general principles involved in the production of bisulphide of carbon, (2) to describe briefly,

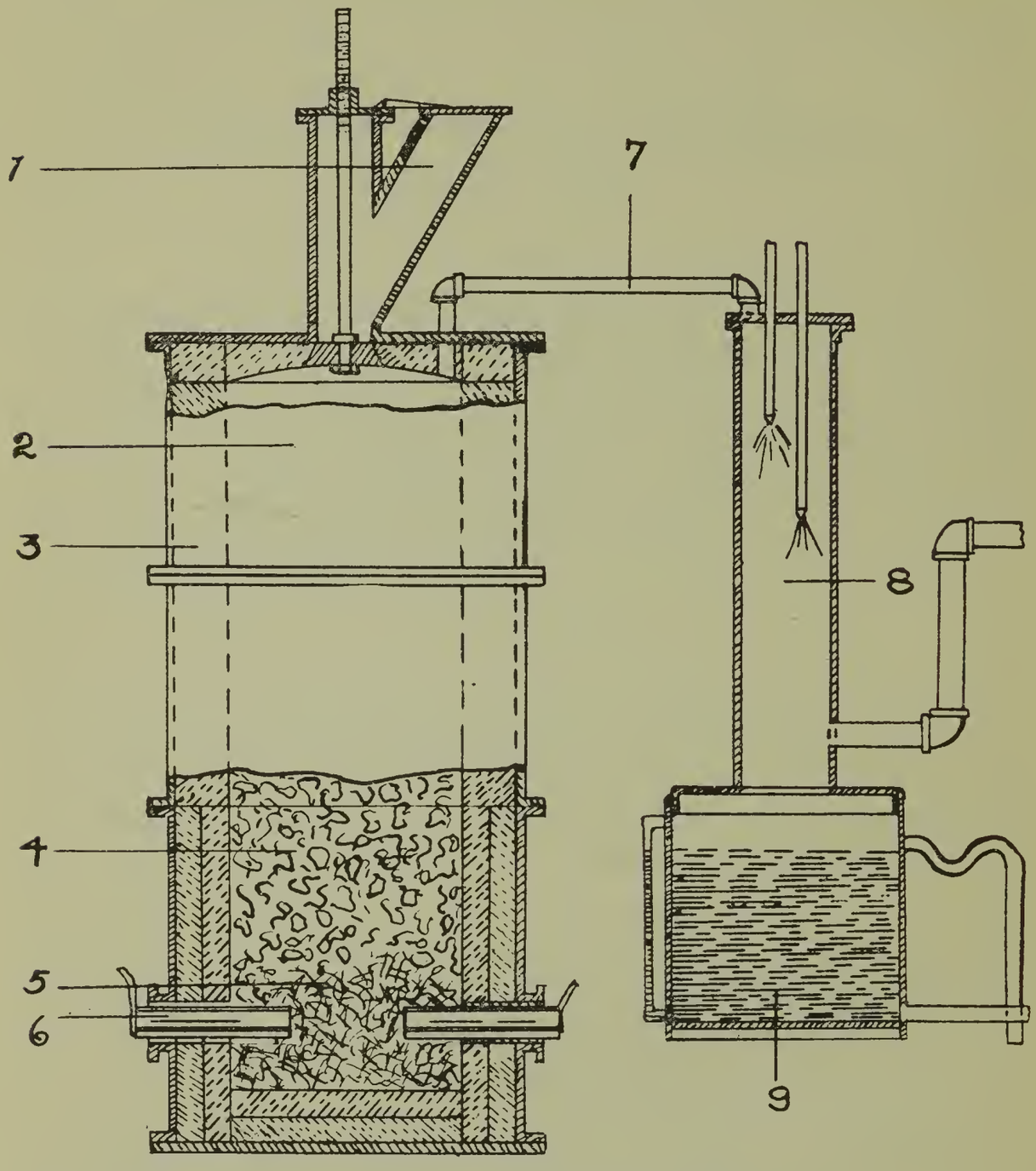


FIG. 1. Carbon Bisulphide Process

1. Charcoal Hopper
2. Furnace
3. Refractory Lining
4. Charcoal
5. Resistance Carbon
6. Electrode
7. Delivery Pipe
8. Condenser
9. Product

but specifically, the process under consideration, and (3) to give some data and calculations covering the process.

Large-scale production of carbon bisulphide is based upon a direct union of two elementary substances, carbon and sulphur,

such a union taking place from 600° to 1,000° C. At these reaction temperatures the sulphur is obviously present as a vapor and the unreacted carbon exists as an incandescent solid. Care must be used in selecting the type of carbon for successful operation. In the writer's experience, gas coke, anthracite coal, and other forms of dense carbon have proved of little use. Best results are possible with a reasonably good grade of willow or birch charcoal, which has a low ash content.

It is important that both sulphur and carbon employed be as dry as practicable. Water brought into the furnace as moisture in the sulphur reacts with the sulphur in the high-temperature zone, forming hydrogen sulphide and other volatile sulphur compounds. These side reactions evidently convert sulphur into useless products at the expense of some heat.

Water present in the charcoal delivered to the furnace is usually distilled from the furnace at a temperature lower than that needed for reaction with sulphur. This is due to the fact that charcoal is usually introduced into the furnace at the upper low-temperature zone in order to conserve heat by employment of countercurrent principles. This calcination of charcoal results in a certain small loss of heat as will be discussed later. It is also of importance to specify a well-burned charcoal. A poorly burned product contains substantial amounts of hydrocarbons which cause loss of both heat and sulphur, due to the formation of useless sulphuretted compounds, which distill off with the carbon bisulphide. In practice it has been found profitable at times actually to dry and reburn some of the charcoal purchased before putting such charcoal into the furnace.

Fig. 1 shows diagrammatically the general layout of the installation under discussion. The furnace consists of a cast-iron shell lined with a suitable grade of refractory. Provision is made for water-cooled electrodes, through which power is furnished from a two-phase 440-volt A. C. line. Transformers and switchboard allow voltage changes in 10-volt steps, such changes being made either to control production or to adjust total power input as the internal electrical resistance of the heating bed varies from time to time.

A resistance bed of broken arc-light carbon is distributed over

the entire cylindrical space between the electrodes. The heat generated is conveyed from the incandescent bed of resistor carbon to the charcoal above.

Sulphur is fed into the furnace from a melting kettle. It is fed through a liquid seal and delivered near the center of the hot zone, where it is vaporized instantly and reacts with the hot charcoal present.

Charcoal is introduced periodically as needed by means of a suitable hopper through the top of the furnace shell. Carbon bisulphide, hydrogen sulphide and other sulphur compounds leave the furnace and enter a condenser where the bisulphide is recovered, and the impurities are washed out continually by means of overflow water.

Attempts have been made to control the temperature of the furnace by means of pyrometers. Peep holes, however, have proved fully as satisfactory, and represent considerably less maintenance costs. The usual maximum temperature is about 1,000° C.

The unit diagramed above will produce one ton of carbon bisulphide in twenty-four hours with a power consumption of 0.5 to 0.7 Kw.H. per pound of washed material recovered. The principal losses of electrical heat and chemicals may be listed as follows:

1. Radiation of heat from surface of furnace including electrode losses.

2. Loss of sensible heat in exit vapors.

3. Loss of heat due to melting and vaporization of sulphur which leaves the furnace as unreacted sulphur and worthless sulphur compounds.

4. Loss of chemicals accompanying heat loss listed under 3.

5. Loss of carbon bisulphide due to leaks and solution in wash water.

In calculating distribution of heat losses, it is important to have available values for the chemical losses which represent heat consumption without the equivalent yield of product. It is fair to estimate a sulphur loss represented by items 4 and 5 as totalling 20 percent of the original sulphur fed to the furnace.

This is equivalent to an 80-percent yield of washed carbon bisulphide, based on original sulphur used, and must be accompanied by an additional 20-percent power consumption over that theoretically required for the production of carbon bisulphide actually recovered.

Knowing the radiating surface, average shell temperature, and the recovery of carbon bisulphide per twenty-four hours, it is possible by making a reasonable assumption for the heat-conductivity coefficient to estimate the heat loss due to radiation. Operating conditions at the plant considered warrant accepting as reasonable the value, $K = 2$.

In order to calculate thermal efficiency, it is necessary to know the theoretical number of heat units needed for the formation of a unit weight of carbon bisulphide. It is also essential that we know the heat requirements for each of the steps of the reaction in question. This involves tabulation of data on latent heats, specific heats, and heat of formation. Unfortunately, there are some discrepancies in physical constants reported, and it has been deemed advisable to record the values found in standard compilations. Such values are given in detail in the appendix. As far as the writer was able to ascertain, no direct measurement of specific heat of sulphur vapor has ever been made. There appears to be an agreement in values given for heat of formation of carbon bisulphide, starting with solid sulphur and carbon and finishing with gaseous carbon bisulphide. Koref has calculated from equilibria data the heat of formation of carbon bisulphide, starting with sulphur vapor, and has shown that such a reaction is exothermic rather than endothermic, as is the case when solid sulphur is used. The vaporization of the sulphur prior to its reaction with carbon demands enough heat to cause a change from an exothermic to an endothermic process.

Mellor gives the following conception of the equilibria involved in raising sulphur to 1,000° C. This summarizes in qualitative manner the results of the investigations of Smith and others during the past thirty years.

$$\underset{\text{Solid forms.}}{\overset{94.5^\circ}{S\alpha \leftrightarrows S\beta}} \quad \overset{120^\circ}{\leftrightarrows} \quad \underset{\text{Liquid forms.}}{\overset{160^\circ}{S\lambda \leftrightarrows S\mu}} \quad \overset{444.5^\circ}{\leftrightarrows} \quad \underset{\text{Gaseous forms.}}{\overset{1{,}000^\circ}{S_8 \leftrightarrows 4S_2}}$$

It is evident from this that the thermal data required include (1) the heats of conversion of S$\propto$ (rhombic) to Sβ (monoclinic), (2) the heat of fusion of sulphur, (3) the heat of conversion of Sλ to Sμ, (4) the heat of vaporization of sulphur, (5) the heat of dissociation of S_8 to S_2, and (6) specific heat data for sulphur extending over the range, 20-1,000° C.

It is impossible to calculate exact thermal requirements for each of these steps since we have no data for specific heat of gaseous sulphur, much less for the heat of dissociation of S_8 to S_2. Bearing in mind, however, that our distribution of heat losses must necessarily be only approximate we may simplify the above course of events and, by making certain allowable assumptions, arrive at a value which will be well within the precision limits of the entire problem. The steps simplified may be taken as:

$$\underset{20^\circ\text{ C.}}{\text{S (solid)}} \rightarrow \underset{120^\circ\text{ C.}}{\text{S (liquid)}} \rightarrow \underset{440^\circ\text{ C.}}{\text{S (gaseous)}} \rightarrow \underset{1{,}000^\circ\text{ C.}}{\text{S (at 1,000° C.)}}$$

Based on constants listed in the appendix, these three steps from solid, to liquid, to gas, to high temperature vapor show an investment of heat units for 64 grams of sulphur amounting to

$$1{,}750 + 29{,}400 + 10{,}700^{(3)}\text{ cal.} = 41{,}850\text{ cal}^{(4)}.$$

The heat required to raise the equivalent 12 grams of carbon from 20° C. to 1,000° C. is calculated as 3,530 cal[5]. It is evident that the sum of calories represented by these two preparatory steps does not indicate the heat units expended in forming the equivalent amount of carbon bisulphide, inasmuch as there is a return of heat due to the exothermic vapor reaction, as well as a return of heat to the entire system due to a cooling down of reaction products to about 200° C.

Thomsen's value of — 26,000 cal. for the heat of formation of gaseous carbon bisulphide, and Koref's calculated value of + 12,500 (from sulphur vapor) are quite consistent with the above heat values.

For purpose of heat-loss distribution, we must estimate the heat lost due to sulphur which has been vaporized but not con-

[3] Assuming 0.3 for sp. ht. of gaseous S.
[4] See appendix "B".
[5] See appendix "C".

verted to carbon bisulphide. Such by-product sulphur leaves the furnace at comparatively low temperatures and would not represent a loss of 41,850 cal. per 64 grams. It is safe to omit the super-heating effect of the vapor thus reducing the loss to 31,150 cal. per 64 grams of sulphur lost. A second subtraction of 1,750 cal. must be made in calculating electric heat loss, inasmuch as the solid sulphur is warmed up and melted by steam outside of the furnace. With a 20-percent loss of original sulphur fed to the furnace, this electric heat loss amounts to 97,000 cals[6]. per kilogram of product.

Loss of heat due to vaporization of water from charcoal containing 5 percent moisture is a small item amounting to only 5,000 cal. per kilogram of product[7].

Radiation of heat from the furnace shell is quite the largest single heat loss realized. The units under consideration have about 320 sq. ft. (29.7 sq. m.) radiating surface. The average shell temperature approximates 100° C. With a room temperature of 20° C. and a conductivity factor of $K = 2$[8], the radiation loss totals 610,000 cal. per kilogram of product[9].

The heat requirements for the production of 1 kilogram of CS_2 in the furnace described above may be summarized as follows:

1.	Heat of formation of 1 kilo finished CS_2[10]....	320,000 cal.
2.	Loss due to drying charcoal.....	5,000
3.	Loss of heat due to subliming S, which leaves furnace in worthless form.....	97,000
4.	Radiation loss	610,000
	Total electric heat input.....	1,032,000 cal.

The tabulated heat balance indicates a thermal efficiency within the furnace amounting to about 31 percent. Converting calories to Kw. H., it is possible to express our results as 1 kilogram of carbon bisulphide produced per 1.20 Kw. H., or 1 lb. per 0.73 H. P. H. These values agree well with actual operating data.

It is quite evident that the largest loss of power is due directly to radiation losses from the furnace. Any increase in capacity of

[6] See appendix "D".
[7] See appendix "E".
[8] K = B.t.u./sq. ft./°F./hr.
[9] See appendix "F".
[10] See appendix "G".

the furnace tends to lower the percent radiation loss and increase the efficiency. The maximum capacity or output per unit time is limited by the maximum allowable sulphur sublimation loss. A point may be reached where added load may increase prohibitively the cost of operation due to loss of chemicals, as well as increased maintenance costs. With current prices of chemicals and hydro-electric power, it may actually prove more profitable to operate the furnace at a somewhat lower thermal efficiency, and to sacrifice efficiency for equivalent financial return.

SUMMARY.

1. A comparatively recent process for the manufacture of carbon bisulphide is described.

2. Actual plant data indicate that these units operate with a reasonably fair thermal efficiency.

3. An approximation of thermal losses is submitted.

In conclusion I wish to acknowledge the valued assistance rendered by Mr. Gordon Cave, who assembled and reviewed critically all references available pertaining to chemical and physical constants.

Appendix A.—Table I.

Carbon Bisulphide.

Heat of Formation, Small Calories per Gram-Atom or Gram-Molecule.

Substance	Condition	Constant	Authority	Compiler	Original Source	Method of Determination	Date
Carbon Bisulphide	Vapor from amorphous carbon and rhombic sulphur	—26010	J.Thomsen	Dammer Landolt-Börnstein-Roth	Jahrsberichte, 1883, 159; 1885, 183 Thomsen's Researches, **2**, 411. German edition	Constant pressure	1883-1885
Carbon Bisulphide	Vapor from amorphous carbon and rhombic sulphur	—25430	J.Thomsen	Dammer	Jahrsberichte, 1883, 159; 1885, 183 Thomsen's Researches, **2**, 411. German edition	Constant volume	1883-1885
Carbon Bisulphide	Vapor from charcoal and S_2 vapor	+12500	Koref	C. A., **4**, 1412	Z. anorg. Chem., **66**, 73-92	Calculation from equilibrium constants and equation of the reaction isochor	1910
Carbon Bisulphide	Liquid from amorphous carbon and rhombic sulphur	—19610	J.Thomsen	Landolt-Börnstein-Roth	Thomsen's Researches, **2**, 411. German edition	Constant pressure	1883-1885
Monoclinic Sulphur	From rhombic sulphur at 95.6°.	—81	Reicher	Landolt-Börnstein-Roth	Inaugural diss. Amsterdam 1883, 76; Zeit. Kryst., **8**, 593	Calculated	1883
	From rhombic sulphur	—86	Tammann	Landolt-Börnstein-Roth	Zeit. anorg. Ch., **63**, 291	Calculated	1909
	From rhombic sulphur at 96°.	—105	Kruyt	Landolt-Börnstein-Roth	Chem. Weekbl. 1911, 647	Calculated	1911
Sulphur μ	From sulphur λ	—420	Lewis & Randall	Landolt-Börnstein-Roth	J. A. C. S., **33**, 487.		1911

Appendix A.—Table II.

Carbon Bisulphide.

Latent Heat in Small Calories per Gram-Atom or Gram-Molecule.

Substance	Condition	Constant	Authority	Compiler	Original Source	Date
Sulphur	Fusion (115°)	299.761 300.338	Person	Castell-Evans Landolt-Börnstein-Roth	Ann. chim. phys. (3), **21**, 333	1847
Sulphur monoclinic	Fusion (119°)	330.	Wigand	Landolt-Börnstein-Roth	Zeit. ph. Ch., **63**, 273	1908
Sulphur S	Vaporization (316°)	11,605.72 11,580	Person	Castell-Evans Landolt-Börnstein-Roth	Pogg. Ann., **70**, 310, 386, possibly from Ann. chim. phys.	1847
Carbon bisulphide	Vaporization (0°)	6850	Regnault	Landolt-Börnstein-Roth	Mem. de Paris, **26**, 761, 811, 819, 829, 835, 849, 857, 913	1862
Carbon bisulphide	Vaporization (0°)	6810	Winkelmann	Landolt-Börnstein-Roth	Wied. Ann., **9**, 208, 358	1880
Carbon bisulphide	Vaporization (14.1°)	6610	Koref	Landolt-Börnstein-Roth	Ann. Phys. (4), **36**, 56	1911
Carbon bisulphide	Vaporization (46.1°)	6380	Wirtz	Landolt-Börnstein-Roth	Wied. Ann., **40**, 446	1890
Carbon bisulphide	Vaporization (46.2°)	6600	Andrews	Landolt-Börnstein-Roth	London Chem. Soc., **1**, 27	1849
Carbon bisulphide	Vaporization (46.6°)	8050	Person	Landolt-Börnstein-Roth	Pogg. Ann. **70**, 310, 386, possibly from Ann. chim. phys.	1847

Appendix A.—Table III.

Carbon Bisulphide.

Specific Heat in Calories per Gram per °C.

Substance	Range	Constant	Authority	Compiler	Original Source	Date
Sulphur 2 yrs. after fusing	15-97°	0.1764	Regnault	Castell-Evans		
Sulphur, rhombic	17-45°	0.163	Regnault	Castell-Evans		
Sulphur, liquid	119-147°	0.2346	Person	Castell-Evans		
Sulphur, liquid	160-201°	0.279	(Deysey) (Dussy)	Landolt-Börnstein-Roth	Compt. rend. **123**, 305	1896
Sulphur, liquid	160-233°	0.300	(Deysey) (Dussy)	Castell-Evans		
Sulphur, liquid	160-264°	0.300	(Deysey) (Dussy)	Castell-Evans		
Sulphur, liquid	201-233°	0.331	(Deysey) (Dussy)	Landolt-Börnstein-Roth	Compt. rend. **123**, 305	1896
Sulphur, liquid	233-264°	0.324	(Deysey) (Dussy)	Landolt-Börnstein-Roth	Compt. rend. **123**, 305	1896
Sulphur, rhomb.	0-32°	0.1719	Wigand	Landolt-Börnstein-Roth	Ann. d. Phys. (4), **22**, 64	1907
Sulphur, rhomb.	0-95°	0.1751	Wigand	Landolt-Börnstein-Roth	Ann. d. Phys. (4), **22**, 64	1907
Sulphur, rhomb.	23-92°	0.1759± 5%	Kurbatov	C. A. **5**, 607	J. Russ. Phys. Soc.,**41**, 311-2	1909

Appendix A.—Table IV.

Carbon Bisulphide.

Specific Heat in Calories per Gram per °C.

Substance	Range °C.	Constant	Authority	Compiler	Original Source	Date
Carbon bisulphide	0	0.23523	Regnault	Castell-Evans Landolt-Börnstein-Roth	Mem. de l'Acad., **26**, 262	1862
Carbon bisulphide	0	0.22958	Hirn	Castell-Evans		
Carbon bisulphide	18	0.242	Forch	Landolt-Börnstein-Roth	Ann. d. Phys. (4), **12**, 202	1903
Carbon bisulphide	30	0.24012	Regnault	Castell-Evans Landolt-Börnstein-Roth	Ann. chim. phys. (4), **10**, 32	1867
Carbon bisulphide	30	0.23938	Hirn	Castell-Evans		
Carbon bisulphide	30	0.2388	Hirn	Landolt-Börnstein-Roth	Ann. chim. phys. (4), **10**, 32	1867
Carbon bisulphide	60	0.24897	Hirn	Castell-Evans		
Carbon bisulphide	80	0.260	Sutherland	Castell-Evans Landolt-Börnstein-Roth	Phil. Mag. (5), **26**, 298	1888
Carbon bisulphide	100	0.26168	Hirn	Castell-Evans		
Carbon bisulphide	120	0.276	Sutherland	Castell-Evans Landolt-Börnstein-Roth	Phil. Mag. (5), **26**, 298	1888
Carbon bisulphide	160	0.2882	Hirn	Landolt-Börnstein-Roth	Ann. chim. phys. (4), **10**, 32	1867

APPENDIX B.

Note:—All calculations were made with slide rule.

Calculations for bringing 64 grams or 2 gram atoms of sulphur from 20° C. to 1000° C.

1. 20° C. to 120° C.
   (64 g.) (0.18) (100°) = 1150 cal.
2. Fusion.
   2 gram atoms x 300 cal. = 600 cal.
3. Heating liquid sulphur.
   (64 g.) (444° — 120°) (0.3) = 6240 cal.
4. Vaporization of sulphur.
   2 x 11,580 = 23,160 cal.
5. Heating sulphur vapor to 1000° C.
   Assume sp. ht. of vapor = 0.3
   (64 g.) (1000° — 444°) (0.3) = 10,700 cal.

Total = 41,850 cal. needed to bring 64 grams of sulphur to 1000° C.

Note:—In the furnace described, the melting is done outside the furnace by steam. This leaves about 41,100 cal. to be furnished by electric heat.

APPENDIX C.

To heat 12 grams of carbon from 20° to 1000° C.
(12) (1000 — 20) (0.3) = 3530 cal.

All this heat is supplied electrically.

APPENDIX D.

Electric heat loss due to 20 percent loss of sulphur in process.

Heat loss per 64 grams of sulphur so rendered worthless =
41,850 — 10,700 — 1750 = 29,400 cal.

With 80 percent yield of carbon bisulphide based on sulphur, heat loss in furnace = $\frac{64,\ (1000)\ (0.20)\ (29,400)}{76 \qquad (0.80) \quad (64)}$ = 97,000 cal. per 1000 g. CS_2 produced.

APPENDIX E.

Electric loss due to distilling of moisture from charcoal.

$\frac{12\ (1000)\ (0.05)\ (608)}{76 \qquad (0.95)}$ = 5000 cal. per 1000 g. of CS_2 produced.

APPENDIX F.

Radiation loss from furnace per kilo. of CS_2 produced.

$K = 2$ B. t. u.

$K = 905$ cal. per sq. ft. per hour per °C.

Production of furnace = 2000 lb. per 24 hr.

Production of furnace = 83.5 lb. per hour.

1 kilo. production requires 0.0263 hour.

Furnace surface = 320 sq. ft.

Average temperature of furnace surface = 100° C.

Room temperature = 20° C.

Then: Heat loss =

(320) (80) (905) (0.0263) = 610,000 cal. per kilo. of CS_2.

APPENDIX G.

Heat of formation of 1000 grams carbon bisulphide starting with liquid sulphur and ending with gaseous carbon bisulphide =

$$\frac{(1000)\ [(-26{,}000) + (1750)]}{(76)} = -320{,}000 \text{ cal.}$$

DISCUSSION.

COLIN G. FINK[1]: Is there any chance of the formation of an oxysulphide, or an intermediate compound? Are there any other compounds besides the carbon bisulphide formed during this process? Your coke is never a pure carbon; it always contains an appreciable quantity of moisture and other impurities.

GEO. A. RICHTER: We do experience that trouble, but it has not really interfered with the process. We take the charcoal as it comes and always calcine it beforehand, the idea being to rid it of as much moisture as possible and also to remove the major portion of hydrocarbons present. In spite of that, we get the oxysulphides, also some sublimed sulphur, but with this type of open condenser our hydrogen sulphides and also the sulphur are automatically removed. The only impurity in the product, that is

[1] Consulting Electrometallurgist, New York City.

taken into such a condenser, is really dissolved sulphur and that can be taken care of, if necessary, in subsequent operations, such as distillation.

Periodically the water could be discarded or neutralized with a little lime, which we sometimes do.

G. S. WHITBY[2]: Is all the carbon bisulphide now manufactured in electric furnaces?

GEO. A. RICHTER: I feel quite certain that one or two concerns in the country are still using a gas-fired retort type.

C. G. SCHLUEDERBERG[3]: What is the output of a plant of that type?

GEO. A. RICHTER: In a plant such as I have in mind, we have four units of this type that normally produce about five tons of carbon bisulphide in twenty-four hours.

COLIN G. FINK: How does this furnace compare in efficiency with that furnace of E. R. Taylor?

GEO. A. RICHTER: The Taylor furnace is a larger furnace and according to the figures given in previous papers the efficiency of such a furnace is about 35 percent; this one is nearer 31 percent.

M. A. HUNTER[4]: At what temperature do the CS_2 vapors leave the furnace?

GEO. A. RICHTER: The carbon bisulphide vapors leave at about 100° C.

M. A. HUNTER: And how do you prevent the outlet tube in the condenser from clogging up with sulphur?

GEO. A. RICHTER: In the outlet tube we have steam-jacketing, but I do not believe we have used that more than once or twice a year. Sulphur sublimation is not a serious difficulty.

M. A. HUNTER: Another question which arises in my mind is, how do you control the rate at which you send your sulphur into the furnace? By hand?

[2] Dept. of Chem., McGill University, Montreal, Canada.
[3] Asst. to Mgr., Supply Dept., Westinghouse Elec. & Mfg. Co., E. Pittsburgh, Pa.
[4] Rensselaer Polytechnic Inst., Troy, N. Y.

GEO. A. RICHTER: That is done entirely at the discretion of the operator. By hand.

M. A. HUNTER: If he puts in too much, what will happen?

GEO. A. RICHTER: If he puts in too much sulphur, his temperature in the furnace will drop somewhat and he will simply have to hold up for an hour, feeding in more slowly until the equilibrium conditions are again established.

We spent quite a bit of money with different types of thermometer-pockets, but at present, and for a long time, we have depended entirely upon the eye, and I believe the average temperature is pretty close to 1,000° C., hot zone.

R. W. DAVIS, JR.[5]: How do the mineral constituents of the charcoal emerge from the furnace?

GEO. A. RICHTER: The accumualtion of ash from the charcoal is really quite small. About every six or eight months, if nothing else has interfered with the operation of the furnace, the normal procedure would be to open up the furnace, through a suitable manhole in the bottom, and rake it clear, but I do not recall any time that the furnace has been shut down because of accumulation of ash between the electrodes.

[5] Jenkintown, Pa.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 22, 1922, President Schlueder-berg in the Chair.

ELECTROSMOSIS AND ELECTROPHORESIS, TWO DEFINITIONS.[1]

By Oliver C. Ralston.[2]

Abstract.

The terms "electrosmosis", "electrophoresis", "cathodophoresis" and "anodophoresis" are proposed (1) to replace a large number of other words, some of which are incorrectly used and all of which are awkward; (2) to gain uniformity of nomenclature in conformity with the two words "electrolysis" and "electrostenolysis."; and (3) to provide single descriptive nouns, which when properly modified can be used as verbs, adjectives or participles that easily displace present clumsy phrases.

The purpose of this note is to call attention to an exasperating confusion of terms in the literature that deals with electro-capillary phenomena, the electric double layer at phase boundaries and in colloid chemistry. The four following words should cover all general cases where an electric current is passed through a fluid medium, with or without a diaphragm, with or without the presence of other solid, liquid, or gaseous particles other than the electrodes or on the electrodes:

Electrolysis.
Electrosmosis.
Electrophoresis.
Electrostenolysis.

Nearly all the roots used in these words are of Greek origin. Electrolysis, for instance, is divided into electro-and-lysis from roots meaning "by means of electricity" and "loosening, dissolu-

[1] Manuscript received August 4, 1922.
[2] Berkeley, Calif.

tion or destruction" respectively. It is therefore well to consider first the meanings of portions of a few words.

Cath-	down or away.
-ode	way or path.
An-	up or toward.
-ode	way or path.
Os-	mouth or pore (Latin).
-mosis	push or impulse.
Endos-	within.
-mosis	push or impulse.
Cata-	down or away.
-phoresis	bearing or carrying.
-sis	suffix meaning process or state.
-osis	suffix meaning process or state.

With these few roots and their meanings it is now possible to discuss the above four words, which are proposed in the interest of obtaining uniform nomenclature, with a minimum of change from present practice and without inventing completely new words.

Electrolysis is a term universally accepted as meaning the act or process of chemical decomposition by means of the electric current.

Electrosmosis is proposed by the writer to supplant such terms as electric osmose, electrical endosmose, electric endosmosis, electro-osmosis, etc. All of these terms mean the passage of liquids through diaphragms (osmosis), due to the application of electrical forces. They are all in use, but all are somewhat awkward when used otherwise than as nouns. If the noun "electrosmosis" is adopted, it can be modified to the verb "electrosmoze" to correspond to the verb "electrolyze".

Electrophoresis is proposed to supplant a number of words that have been sadly misapplied, but whose use has almost become correct through common (mis)usage. By electrophoresis is meant the travel, transport or "wandering" of a particle of solid, liquid, or gaseous matter suspended in a mobile medium, liquid

or gaseous, when a uni-directional electric stress is applied. At the present time "cataphoresis" is the word usually heard in this connotation, although "electrophoresis" has been used by a few discriminating writers.

The objection to the use of the word "cataphoresis" is that most of the particles suspended in aqueous solutions are negatively charged and migrate toward the anode, whereas the prefix "cata" or "cath" is already associated with "cathode" and "catholyte." A few writers have therefore tried to apply "cataphoresis" only to cases where particles wander toward the cathode, and have invented "anaphoresis" to apply to the usual case of wandering toward the anode. They were the ones who invented "electrophoresis" as the general phenomenon. Due to the wide use of "cataphoresis" it would seem unwise to try to force its use for a case of "electrophoresis" in which the particle wanders toward the cathode, a direction which is just the opposite of 90 percent of the cases of so-called cataphoresis. Rather it seems wiser to adopt a term somewhat different in spelling, enough different to force recognition of the true meaning, and yet not enough different to need definition. Therefore:

Cathodophoresis is proposed to mean migration of suspended particles towards the cathode when under the influence of a uni-directional current.

Anodophoresis is proposed to mean migration to the anode.

A further discussion of the possibilities of the use of the term "electrophoresis", as defined above, will show its great usefulness. It need not apply alone to colloidal solutions, but it can also apply to smokes, mists and fumes. The Cottrell electrical precipitation process has long lacked a single word to describe correctly its phenomena. It is permissible to speak of "electrophorizing" these suspensions of solid or liquid particles in gases. We can also "electrophorize" emulsions of water in crude petroleum, a process which has long wanted a name, and is now in such large-scale use that a less accurate name is likely to be attached to it if we do not act to embody properly these ideas in suitable words.

Electrostenolysis is a term used to designate the deposition of certain metals in small capillary pores of certain diaphragms when

solutions of these metals are electrolyzed. This is a rather obscure phenomenon but its name is fortunately quite correctly derived and used. However, the definition should not be restricted to the deposition of m e t a l s in pores of diaphragms, as someone may discover methods of depositing other elements or groups in like manner.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 22, 1922, President Schlueder-berg in the Chair.

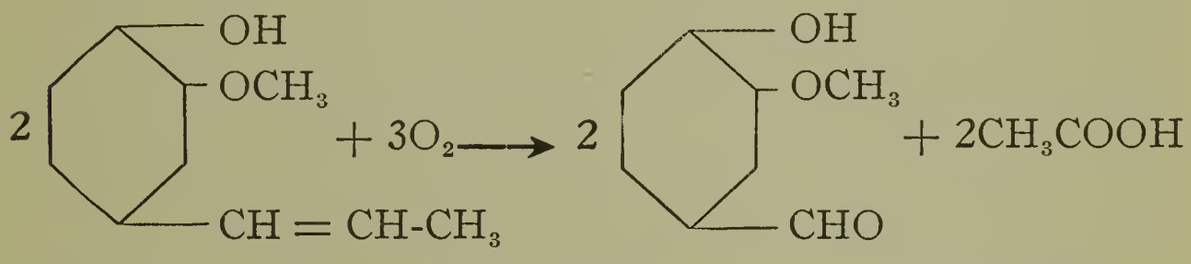
ELECTROLYTIC OXIDATION OF ISOEUGENOL.[1]

By Alexander Lowy and Catherine M. Moore.[2]

Abstract.

German Patent (D. R. P. 92007), which describes a method for the preparation of vanillin by the electrolytic oxidation of isoeugenol, was investigated. A series of experiments, using NaOH as the electrolyte was conducted, and in every instance a negative yield was the result. Vanillin itself was found to oxidize readily electrolytically, and even if formed by electrolytic oxidation it would be immediately carried over into other products. Then a series of experiments was carried out, using H_2SO_4 as the electrolyte. Here again the yields were all negative. Hence, it was concluded that if vanillin is produced by the electrolytic oxidation of isoeugenol, a totally different condition must prevail.

In consulting the literature of isoeugenol, it was found that in many cases statements were made to the effect that vanillin could be prepared by the electrolytic oxidation of the sodium salt of isoeugenol, according to the equation—



All of these statements,[3] with the exception of one,[4] referred

[1] Manuscript received August 16, 1922.

[2] Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa.

[3] Foerster "Elektrochemie," **1**, 786.
Hale, "Applications of Electrolysis in Chemical Industry," p 339.
Beilstein, "Handbuch der Organischen Chemie" Ergärzungsband, **3**, 73.
Haber und Moser, "Elektrolytische Prozesse", p. 78.
Loeb und Lorenz, "Electrochemistry of Organic Compounds," p. 202.

[4] Thorpe, "Dictionary of Applied Chemistry," V. 614, referred to English Patent 1624 (1895), which is the same patent as D. R. P. 92007 (1895) taken out by J. Y. Johnson in England.

to a German Patent (D. R. P. 92007, 1895) as the source of their information. Since no other experimental details could be found in the literature for the preparation of vanillin by this method, a study of the process was made, essentially as outlined in the patent. A photostat copy of the specifications of the patent was procured from the United States Patent Office, a translation of which follows.

IMPERIAL PATENT OFFICE
Patent No. 92,007
Class 12: Chemical Apparatus and Processes
Published April 3, 1897

Dr. F. von Heyden Nachfolger (Successor) of Radebeul in Dresden. Procedure for the Preparation of Vanillin by means of Electrolysis, Patented in the German Empire, January 17, 1895.

"We have discovered an extraordinarily simple method for the preparation of vanillin, when we subjected isoeugenol to the electric current. During this electrolysis the oxidation of isoeugenol to vanillin takes place at the anode. It is expedient to use the alkali salt of isoeugenol and to carry out the electrolysis in a double cell, so that the anode dips into the isoeugenol salt, while as catholyte any good conducting, alkaline liquid is used, most advantageously, dissolved sodium hydroxide or potassium hydroxide or carbonate. During the electrolysis the alkali metal passes from the anode to the cathode, and is replaced by the addition of alkali, either before or during the electrolysis.

"For example: The anode cell is charged with a liquid, which contains about 15 percent of isoeugenol in an excess of caustic soda. The cathode cell is filled with a 10 to 20 percent caustic soda solution. A current of about five volts and six amperes is passed through the cell. The anode surface and the cathode surface can, for example, amount to 0.0046 square meter, so that with six amperes the current density amounts to 1304 (figured to one square meter). Of course these numbers can vary within wide limits. It is advisable during the electrolysis to heat gently; for example, to 60°C. The course of the electrolysis is followed by withdrawing test portions of the anode liquid and approximately determining the contents of vanillin and isoeugenol or by titrating the catholyte. By stopping the current the conversion of the isoeugenol into vanillin can be controlled. After stopping the electrolysis, a new anode liquid can be prepared from the cathode liquid by the addition of isoeugenol, while the anode liquid is acidified and extracted with ether. The ether contains vanillin and also some unchanged isoeugenol. The vanillin is extracted from the ether solution by shaking with bisulfite. The vanillin-bisulfite solution is further worked according to known methods.

"PATENT CLAIM.—The procedure for the preparation of vanillin by the electrolysis of isoeugenol salts."

The original purpose of this investigation was to ascertain if vanillin could be made by this process, (electrolytic oxidation of isoeugenol) and, if so to work out the experimental details for the process, as the patent specifications do not denote kind of electrodes used, length of time of electrolysis, stirring arrangements, etc. Since only a trace of vanillin was obtained by oxidizing

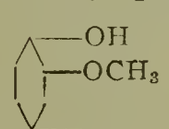
isoeugenol according to the details of the patent, it became the purpose of the investigators to find out if the yield of vanillin could be increased by varying the conditions.

It is not surprising that only a trace of vanillin was obtained, when a study is made of the compound isoeugenol and its oxidation possibilities. It contains an OH group and a $-CH = CH-CH_3$ group, both of which are very susceptible to oxidation. Considering first the unsaturated side chain, a series of products could be obtained:

Coniferyl alcohol.... $R^{(5)}-CH = CH-CH_2OH$
Ferulic aldehyde.....$R-CH = CH-CHO$
Ferulic acid.....$R-CH = CHCOOH$
Vanillin.....$R-CHO$
Vanillyl alcohol.....$R-CH_2OH$
Vanillic acid.....$R-COOH$
Dehydro-divanillin...$(OCH_3)(OH)\ C_6H_2(CHO)$
$(OCH_3)(OH)\ C_6H_2(CHO)$

The chemistry of isoeugenol and vanillin has never been worked out in detail, and of the above mentioned products comparatively little is known.

The compound isoeugenol has an OH group, which would cause it to behave like a phenol. Bartoli and Papsoli[6] when electrolyzing solutions of phenol in potassium and sodium hydroxide, and using electrodes of coke, graphite, and platinum, obtained an acid having the composition $C_7H_6O_4$, which melted at 93°C. When retort coke was used as the positive electrode, an extensive decomposition of the phenol occurred and a resin was formed. On subjecting a neutral solution of potassium phenolate to the action of the electric current they were able to isolate a compound $C_{65}H_{48}O_{22}$, soluble in alkali and precipitated from such solutions by mineral acids. The electrolysis of neutral sodium phenolate solution gave an acid having the formula $C_{29}H_{20}O_8$. Considering all these possibilities, the probabilities of obtaining vanillin by electrolytic oxidation are very poor. Experimental facts showed that even if

[5] R = 

[6] Gazz. Chim. 1884, 14, 103.

vanillin were formed by this method, it would be immediately carried over into other products. Details are given under the experimental part of this paper.

EXPERIMENTAL PART.

1.—Using NaOH as Electrolyte.

The first experiment was carried out in order to duplicate the details given in the German patent.[7] The details of this experiment were as follows:

Thirty grams of isoeugenol were dissolved in 200cc. of a 15 percent solution of NaOH. This solution was used as the anolyte and a 15 percent NaOH solution was used as the catholyte in a porous cup. A platinum gauze anode, with a surface of 0.40 square decimeter, and a platinum wire cathode were used. A current of five amperes and five volts was passed through the cell. During the electrolysis the solution was heated to 60° C. at which temperature the sodium salt of isoeugenol is soluble. A stirring arrangement was used, in order to keep the solution well agitated.

When the current had been passed for five hours, it was turned off and the solution cooled and was carefully acidified with dilute hydrochloric acid, which caused the formation of a brownish gelatinous precipitate. The entire mixture was then extracted with ether, but some of the precipitate did not dissolve in the ether. This insoluble residue was preserved for further experimental work in order to indentify it. The etheral solution was filtered and shaken for some time with sodium bisulfite solution. The sodium bisulfite solution was then separated from the etheral layer, decomposed with dilute sulphuric acid and extracted with ether. Upon evaporating it, a small amount of a brown resinous material, with the odor of vanillin, was obtained.

The product was boiled up with water, and the aqueous extract when evaporated to dryness yielded a small amount of crystalline material with the odor of vanillin. The ether from the first ether extract was distilled off, and a resinous product with odor of isoeugenol remained. This product was steam distilled to remove the isoeugenol, and the residue preserved for further experimental work in order to indentify it.

The above scheme of separation was tried, using pure vanillin,

[7] D. R. P. 92007.

and was found to give almost a quantitative yield. It has been recommended as a quantitative method for the determination of vanillin.

Since only a trace of vanillin was obtained in the above experiment, a series of experiments were made utilizing variable factors. These experiments are recorded in Table I. In none of them was it possible to get even the characteristic test for vanillin, *i. e.*, a blue coloration with $FeCl_3$.

Since only a trace of vanillin was obtained in the above series, an experiment was made to see if vanillin was stable under the conditions mentioned in the patent. Fifteen grams of vanillin were dissolved in 200cc. of 15 percent NaOH solution, and the solution warmed to 60° C., when a pale yellow, clear solution was obtained. The solution was placed in the anode compartment, and electrolyzed under conditions given in experiment 1, Table I.

As soon as the current was turned on, a brown coloration began to form at the anode, and in less than half an hour the entire solution had become brownish black in color. After the current was turned off the solution was cooled and acidified with dilute hydrochloric acid. A brownish black product was obtained, which was absolutely insoluble in ether and water. Not a crystal of vanillin could be recovered.

This simple experiment would seem to prove that if vanillin were formed by the oxidation of isoeugenol according to the method outlined in the patent, it would be immediately carried over into another product. To show that the results just mentioned were not due to the effect of the sodium hydroxide on the vanillin a blank was run, with vanillin in 15 percent caustic solution at 60°C. After heating six hours the solution was acidified and extracted with ether. All of the vanillin was recovered unchanged.

2—Experimental Work on the Resinous Products Obtained in Experiments 1, 2 and 8, Table I.

The ether insoluble product, which was dark brown in color, was first steam distilled, dissolved in NaOH, in which it was very soluble, filtered, and precipitated with dilute hydrochloric acid. The product when first precipitated was gelatinous and difficult to filter; it was dried in a desiccator. The dried product was found

TABLE I.

Electrolytic Oxidation of Isoeugenol.

Using NaOH as Electrolyte

Exp.	Purpose.	Anolyte	Catholyte	Amp.	Volts.	Temp. °C.	Time Hours	Anode and Size	Vanillin	Products
1	To duplicate conditions specified in patent.	30g. isoeugenol in 200cc. 15% NaOH solution	15% NaOH	5	5	55–60	5	Pt gauze 0.40 sq. dm.	Trace	1.5g. ether-insoluble, 12.0g. ether soluble and isoeugenol
2	To find out if composition of anode affected products	As in Exp. 1	15% NaOH	5	5	58–60	4	PbO_2 plate 0.42 sq. dm.	Trace	12g. ether-insoluble, 5.1g. ether soluble and isoeugenol
3	As in Exp. 2	As in Exp. 1	15% NaOH	5	5	60	4¾	Fe wire gauze 0.405 sq. dm.	Trace	In each case obtained an ether soluble resin, an ether insoluble resin and some unchanged isoeugenol
4	Used no stirring to see if stirring affected above results	As in Exp. 1	15% NaOH	5	5	60	5	Pt gauze 0.40 sq. dm.	Trace	As in Exp. 3
5	To see if length of time of electrolysis affected results	As in Exp. 1	15% NaOH	5	5	60–65	2½	Pt gauze 0.40 sq. dm.	Trace	As in Exp. 3

6	To see if length of time of electrolysis in different NaOH concentration affected results	60g. isoeugenol & 20 g. NaOH in 200cc. solution	10% NaOH	5	9–10	60–70	16	Pt gauze 0.40 sq. dm.	None	As in Exp. 3
7	To see if a low current density would affect results	50g. isoeugenol & 20 g. NaOH in 400cc. solution	10% NaOH	1	3.5–5	58–60	8	PbO_2 plate 1.02 sq. dm.	Trace	As in Exp. 3
8	To see if lower current density would affect results	20g. isoeugenol & 11g. NaOH in 200cc. solution	10% NaOH	0.5	3–3.2	60	35	PbO_2 plate 0.50 sq. dm.	Trace	As in Exp. 3
9	To see if lower temperature would affect results	5g. isoeugenol in 300cc. 10% NaOH	10% NaOH	5	8–9	15–20	5	Pt gauze 0.40 sq. dm.	Odor only	As in Exp. 3
10	To see if increasing the concentration of NaOH would affect results	30g. isoeugenol in 200cc. 20% NaOH	20% NaOH	5	5	60	5	Pt gauze 0.40 sq. dm.	None	As in Exp. 3
11	To see if KOH instead of NaOH would affect results	30g. isoeugenol in 200cc. 15% KOH	15% KOH	5	5	60–65	4	Pt gauze 0.40 sq. dm.	Trace	As in Exp. 3

In all these experiments the cathode was platinum wire.

TABLE II.

Electrolytic Oxidation of Isoeugenol.

Using H_2SO_4 as Electrolyte

Exp.	Purpose	Anolyte	Catholyte	Amp.	Volts	Time. Hrs.	Temp. °C.	Anode and Size	Diaphragm	Vanillin	Products
1	Using H_2SO_4 as the electrolyte	10g. isoeugenol in 500cc. 5% H_2SO_4	5% H_2SO_4	2	6–8	7	30	Pt gauze rotating 0.40 sq. dm.	None	Trace	All ether soluble
2	To study effect of increase of concentration of H_2SO_4	10g. isoeugenol in 500cc. 10% H_2SO_4. Used acetone to aid suspension	10% H_2SO_4	2	5–6	10	25–30	Pt gauze 0.40 sq. dm.	Porous cup	None	Obtained only a black charred product
3	As in Exp. 2	10g. isoeugenol in 500cc. 20% H_2SO_4	20% H_2SO_4	2	10–12	..	..	Pt gauze 0.40 sq. dm.	Porous cup	None	20% H_2SO_4 caused charring of isoeugenol
4	To see if increase of C. D. would make a difference	10g. isoeugenol in 500cc. 5% H_2SO_4	5% H_2SO_4	4	8–10	5	40–45	Pt gauze rotating 0.40 sq. dm.	None	Trace	An ether-soluble resinous product & some isoeugenol
5	As in Exp. 4	As in Exp. 4	5% H_2SO_4	6	10–12	5	55–60	As in Exp. 4	None	Trace	As in Exp. 4
6	As in Exp. 4	As in Exp. 4	5% H_2SO_4	5	10–12	5	60–70	Pt wire 0.05 sq. dm.	None	Trace	As in Exp. 4
7	To see if a catalytic agent would promote oxidation	As in Exp. 4 + 0.5 g. ceric sulphate	5% H_2SO_4	5	10–12	5	60	Pt gauze rotating 0.40 sq. dm.	Porous cup	Trace	As in Exp. 4

8	As in Exp. 7	As in Exp. 4 +0.5 g. K_2CrO_4	5% H_2SO_4	5	10–12	5	60	As in Exp. 7	Porous cup	None	As in Exp. 4
9	To see if a PbO_2 anode would affect yield	10g. isoeugenol in 500cc.—5% H_2SO_4	5% H_2SO_4	5	8–10	5	55–60	PbO_2 cylinder rotating 0.42 sq. dm.	Porous cup	Trace	As in Exp. 4
10	As in Exp. 9	As in Exp. 9	5% H_2SO_4	5	8–10	6	60	As in Exp. 9	Porous cup	Trace	As in Exp. 4
11	Used acetic acid to give better suspension to see if that would increase yield	As in Exp. 9	5% H_2SO_4	5	14–18	6	60	Pt gauze rotating 0.40 sq. dm.	Porous cup	Trace	As in Exp. 4
12	To produce ozone and $(NH_4)_2S_2O_8$ at the surface of the anode to see if they would increase yield	10g. isoeugenol in 500cc. saturated $(NH_4)_2SO_4$ solution	50% H_2SO_4	5	14–16	6	20–25	Pt wire 0.05 sq. dm.	Porous cup	Trace	As in Exp. 4
13	As in Exp. 12	10g. isoeugenol in 500cc.—5% H_2SO_4 saturated with $(NH_4)_2SO_4$	5% H_2SO_4	5	14–16	6	20–25	Pt wire 0.05 sq. dm.	Porous cup	Trace	As in Exp. 4

In all these experiments the cathode was platinum wire.

to be insoluble in boiling water, and in ether; soluble in acetone, alcohol, glacial acetic acid, acetic anhydride, giving in each case an intense brown solution.

From none of these solvents would it crystallize, due to its too great solubility. Several other solvents, benzene, toluene, petroleum ether, and ethyl acetate were tried, but in these it was insoluble. Then the product was refluxed with benzene for one hour, when a very small amount of a dark brown oily product was extracted. The remainder of the product was taken up in NaOH again, filtered, precipitated with dilute hydrochloric acid, and again dried. The product was a black amorphous mass, which melted with decomposition between 190° and 200°C.

The ether soluble product was also steam distilled, dissolved in NaOH and precipitated with dilute hydrochloric acid. The product was a light colored flocculent precipitate; this was filtered and dried in a desiccator; it melted with decomposition, commencing at 80°C. An endeavor was made to crystallize this product also, but without success. Some of the product was placed in an oven at about 105°C. and left 14 hours. A brown fused amorphous mass was obtained, which also melted with decomposition, but at a higher temperature than the above product dried in the desiccator.

An effort was made to identify the substance by testing for various groups. It did not give an aldehyde test, either with Schiff's reagent, Fehling's solution, or $NaHSO_3$; nor did it give an acid test, when titrated in alcohol with $N/40$ $Ba(OH)_2$ solution.

It gave no color with ferric chloride solution. One gram of the substance was refluxed for two hours with acetic anhydride, and the reaction mixture poured into water. An oily product was formed, this was boiled up with water, and an amorphous product remained. This product was recrystallized from alcohol. A pale yellow substance was obtained; it melted with decomposition between 115° and 130°C. This seemed to prove that the OH group was present.

A test for the methoxy (OCH_3) group was made according to Hewitt and Moore's modification of the Zeisel method, and the (OCH_3) group was found to be present.

A molecular weight determination was made by observing the rise in the boiling point of acetone, caused by dissolving the substance in it. The molecular weight was found to be 560 to 590.

3—Experiments Using H_2SO_4 as Electrolyte.

Since only a trace of vanillin was obtained in the experiments listed in Table I, further investigation was carried out using sulphuric acid as the electrolyte. Sulphuric acid was chosen in preference to any other acid, because it has frequently been employed in the electrolytic oxidation of organic compounds. The isoeugenol is insoluble in dilute sulphuric acid, but could be maintained in suspension in it, by vigorous stirring, either with a rotating anode or a bell stirrer. Concentrated sulphuric acid caused immediate charring of the isoeugenol, as did 20 percent acid. A series of experiments was carried out using sulphuric acid as the electrolyte, and varying other conditions. The first experiment is described in detail.

Ten grams of isoeugenol were suspended in 500cc. of 5 percent sulphuric acid solution by means of vigorous stirring; this was used as the anolyte. Five percent sulphuric acid was used as the catholyte. A rotating platinum gauze anode of 0.40 square decimeter area was used; and a platinum wire cathode was used. A porous cup was used as the cathode compartment. A current of two amperes and six to eight volts was passed through the cell for seven hours.

During the electrolysis the isoeugenol formed a resinous mass which floated on the surface of the electrolyte. After the electrolysis the mixture was cooled and extracted with ether. The entire product was soluble in ether. The etheral solution was then shaken up with sodium bisulfite solution for several hours. The bisulfite solution was then decomposed with dilute sulphuric acid and extracted with ether. The ether was evaporated and a small amount of resinous material was left, which smelled of vanillin. This material was boiled up with water, and when evaporated to dryness a small amount of crystalline material was obtained. The ether from the first ether extract was distilled off, and a resinous product smelling strongly of isoeugenol was left.

An outline of the experiments conducted is given in Table II. The resinous product obtained in this series of experiments was quite similar to the ether-soluble resin obtained in experiments of Table I. It melted with decomposition, beginning at about 80°C. The product was dissolved in NaOH and precipitated with dilute hydrochloric acid and dried in an oven at 105°C. for 36 hours.

A brown fused amorphous solid was left; it also melted with decomposition between 80° and 120°C.

The compound was tested for sulphur, by fusing with sodium and treating the solution obtained with sodium nitroprusside. The test was negative, and proved that the sulphuric acid did not cause any sulfonation.

To prove that the product obtained was not due to the action of sulphuric acid on isoeugenol, a blank was run, heating isoeugenol at 60°C. for five hours with 5 percent sulphuric acid, as used in experimental work. There was no change, but on prolonged heating at a higher temperature, a reaction did take place, forming a resinous product.

CONCLUSIONS.

1—Since isoeugenol is so susceptible to oxidation, and such a wide variety of oxidation products is possible, and

2—Since vanillin itself is so readily oxidized electrolytically, and

3—Since in every instance, a resinous substance was obtained, it is concluded, that under conditions specified, an appreciable amount of vanillin is not prepared by the electrolytic oxidation of isoeugenol as stated in D. R. P. 92007. Therefore the statements made in the text books, that vanillin can be prepared by this method, should be modified or corrected.

Perhaps derivatives of isoeugenol, such as the acetyl or benzoyl, could be used to produce the desired results.

DISCUSSION.

ALEXANDER LOWY: I may add that on page 274, after the title in the second paragraph, it specifies that "we have discovered an extraordinarily simple method." I may say that we obtained a product having a melting point from 80 to 100°, and we often wondered during the course of the work whether these authors have not taken the melting point as the standard of identification. Just because they obtained a melting point of 80 to 85°, they perhaps thought it was vanillin.

Vanillin has a melting point of 81°, and that is the only connection I can see in regards to his expression, "an extraordinarily simple method."

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 22, 1922, President Schlueder-berg in the Chair.

PREPARATION OF PERCHLORATES BY HEATING CHLORATES.[1]

By Frank C. Mathers[2] and Jacob W. H. Aldred[3]

Abstract.

No variation in the conditions of heating chlorates and no catalysts were found whereby the yield of perchlorate by heating chlorate could be increased. A maximum yield of about 55 percent perchlorate was obtained by heating 1 to 50 grams potassium chlorate for 30 to 60 minutes at 480° to 540° C. Most substances, when added, decreased the yield. The sodium chlorate gave a smaller yield. There seems no possibility that the chemical preparation of perchlorate from chlorate can equal the electrolytic method.

INTRODUCTION.

Possible uses for perchloric acid for preparing electroplating baths, especially for lead, make a cheap source of perchloric acid desirable to electrochemists. This paper gives the results of experiments seeking to increase the yields by heating chlorate under various conditions.

REVIEW.

There have been many researches upon the reactions taking place during the heating of chlorates. The aim in many cases was merely to find the proper equation for the reaction. Potassium and sodium chlorates gave better yields than any of the other chlorates that were tried. Calcium, strontium, lithium, thallium, ammonium, and lead chlorates decomposed to the chloride too easily, or perhaps their perchlorates were too unstable.

[1] Manuscript received April 20, 1922.

[2] Assoc. Prof. Chem., Indiana University.

[3] Research Chemist, Roessler and Hasslacher Chemical Co., St. Albans, W. Va.

This research was undertaken entirely on account of the statement by Fowler and Grant[4] that potassium chlorate heated with silver oxide gave potassium perchlorate and silver. It was thought that perhaps the silver under high pressure of oxygen would act as a catalyst to oxidize the chlorate to perchlorate. Bennett and Mack[5] advanced the theory that the electrolytic preparation of perchlorate was merely an oxidation by active oxygen. They prepared perchlorate by such active oxidizing agents as persulphate, hydrogen peroxide, etc., on aqueous solutions of chlorate. They considered that the experiment by Fowler and Grant with chlorate and silver oxide was a good proof of their theory, but, unfortunately they did not try to duplicate this experiment. This research shows that the silver oxide decreases the yields of perchlorate.

The reactions for the decomposition of a chlorate may be written thus:—

$$4KClO_3 = KCl + 3KClO_4$$
$$2KClO_3 = 2KCl + 3O_2$$
$$KClO_4 = KCl + 2O_2$$

Reaction one should be catalyzed in some way and the others should be suppressed.

The heats of formation of the various reactions are:

$$KCl + 3O = KClO_3 - 11.9 \text{ cal.}$$
$$KCl + 2O_2 = KClO_4 + 7.9 \text{ cal.}$$
$$NaCl + 3O = NaClO_3 - 13.1 \text{ cal.}$$
$$NaCl + 2O_2 = NaClO_4 + 2.4 \text{ cal.}$$

These data show that sodium chlorate evolves more heat by its decomposition than does potassium chlorate, and that the sodium chlorate should be less stable than the potassium chlorate. However, the heat evolved in the change from chlorate to perchlorate is sufficiently great so that it should be possible to catalyze this reaction.

APPARATUS.

An electrical resistance furnace was used. The temperature was accurately controlled by external resistance. A nitrogen filled

[4] Jour. Chem. Soc. 1890, **57**, 272.

[5] Trans. Am. Electrochem. Soc., 1916, **29**, 323; Chem. Eng., 1916, **23**, 200.

thermometer was used for temperatures below 500° C. and a thermocouple for higher temperatures. Glass test tubes were used as containing vessels for the chlorate.

ANALYTICAL METHODS.

A complete analysis was made of each sample after heating. In no case was the perchlorate estimated by difference after determining the chlorate and chloride only. Exceptional accuracy is not claimed for these determinations. The various catalysts frequently caused some difficulties. In many cases there was appreciable loss from spattering of the fused mass by the rapidly evolved oxygen. This error was especially great at the high temperatures. Some error was also caused by changes in the salt through reaction with the containing vessel.

The perchlorate yield was determined as follows: The chlorine present as chloride and chlorate was determined volumetrically with silver nitrate solution after reduction with ferrous sulphate. A separate sample was treated with a little manganese nitrate, for catalyst, and heated to 600°C. The total chlorine in this sample was titrated in the same way and the difference represented the chlorine as perchlorate. This is the standard method. The chlorine present as chloride and chlorate could have been subtracted from the theoretical total chlorine, based upon the weight of chlorate used. However this would have introduced an error if any of the charge had been lost through spattering, etc.

EXPERIMENTAL.

Silver oxide was tried in proportions of 1 : 1 and 1 : 200 in both sodium and potassium chlorate, and the time of heating was varied from one to four hours. The data for one hour heating are given in Table I.

The data for the experiments heated for four hours are like those in Table I, except that the decompositions take place at lower temperatures. This table shows that:

1. The presence of silver oxide very greatly decreases the yields of perchlorate from both the potassium and the sodium chlorate.

2. Sodium chlorate in all cases gives lower yields than the potassium chlorate, due without doubt to the lower stability of the sodium perchlorate.

3. Heating for four hours at 480° C. gave the best yield, 55 percent, of potassium perchlorate but 510° C. for one hour gave the best yield, 31.4 percent, of sodium perchlorate.

4. The idea of Fowler and Grant, and later repeated by Bennett, that silver oxide furnished oxygen to or oxidized the chlorate is false. Every increase in the quantity of the silver oxide used, the lower the yield.

TABLE I.

Silver Oxide Heated with Sodium and Potassium Chlorate. Time, One Hour

	Percent	450°	480°	510°	540°	570°
1 gm. $KClO_3$, blank.	KCl	11.7	33.4	24.5	53.2	80.0
	$KClO_3$	83.4	37.3	32.2	14.0	14.0
	$KClO_4$	2.9	28.3	39.8	30.9	3.8
1 gm. $KClO_3$, 1 gm. Ag_2O	KCl	63.0	87.5	95.7	...	93.3
	$KClO_3$	32.7	0	2.6	...	0
	$KClO_4$	0	9.2	0	...	1.2
1 gm. $KClO_3$, 0.02 gm. Ag_2O.....	KCl	19.5	38.6	61.4	92.8	93.3
	$KClO_3$	73.9	49.0	12.9	2.6	0
	$KClO_4$	3.9	11.5	23.3	0	1.2
1 gm. $NaClO_3$,blank.	NaCl	10.0	12.0	52.5	97.2	...
	$NaClO_3$	83.9	79.4	13.4	0	...
	$NaClO_4$	3.3	5.6	31.4	0	...
1 gm. $NaClO_3$, 1 gm. Ag_2O	NaCl	85.2	94.5	97.1	...	...
	$NaClO_3$	3.2	1.1	0	...	...
	$NaClO_4$	6.6	0	0	...	...
1 gm. $NaClO_3$, 0.02 gm. Ag_2O.....	NaCl	24.2	40.9	97.2	0	...
	$NaClO_3$	62.7	49.1	0	...	...
	$NaClO_4$	9.9	3.4	0	...	...

Red lead, Pb_3O_4, entirely prevented and mercuric oxide, HgO, greatly reduced the perchlorate yields. The data are similar to those already given for silver oxide.

The glass of the containing vessels decreased the yields, probably by catalytic decomposition of the perchlorate. The area of the glass surface of the test tube touched by the fused mass was about 0.59 sq. cm. Some glass slugs, with rounded smooth ends, having an area of about 3.4 sq. cm. were added to each test tube. This six fold increase in glass area in contact with the reacting

mass reduced the yields in the case of both the sodium and the potassium chlorates. The yields were only about 20 percent as large as without the glass slugs.

The greater the quantity of the chlorate heated in any experiment the smaller the area of glass per gram of material heated. This is one reason why the heating of larger quantities of the chlorate gives higher yields. Another effect of heating larger quantities is that a longer time is required for the material to reach the temperature registered by the thermometer or couple, and therefore the decomposition will be less for any maximum temperature the larger the quantity of chlorate used. From these considerations it follows that apparently higher temperatures are

TABLE II.

Heating Potassium Chlorate

Gm. $KClO_3$ heated	Time of heating min.	Temp. °C.	Yield of $KClO_4$ in percent	KCl formed percent
50	30	510	18.4	9.2
50	30	540	54.6	33.9
50	30	575	32.7	57.0
50	30	600	11.8	77.2
1	30	510	53.9	41.2
15	30	510	43.5	49.5
1	60	510	39.8	24.5
1	4 hr.	510	23.1	74.7

used for longer periods of time with the use of larger quantities of the chlorate. Also the smaller the quantity of chlorate used the shorter the time of heating and the lower the temperature. The data supporting the above ideas are given in Table II.

The results with sodium perchlorate were in the same ratio as the above. In every case the decomposition was greater and the yields of perchlorate lower.

It was supposed that caesium and rubidium perchlorates would be more stable than potassium, hence experiments with them were run at the high temperatures of 510° to 570° C. for 1 gm. samples only. Rubidium gave higher yields than caesium, but both were less than with potassium. It is unfortunate that these experiments were tried at these high temperatures where instability prevented anything but low yields.

Sodium chlorate was heated at 360° C. in a closed tube connected with a manometer, in order that any evolution or absorption of oxygen could be detected. There was only a slight increase in volume for a long time. As time went on the rate of decomposition, as shown by the increase in pressure, gradually increased. In another experiment, oxides of nitrogen were introduced into the tube above the sodium chlorate. The decomposition was very rapid and in 2.5 hours the mercury was pushed out of the manometer.

After all of this work had been completed, the paper by Blau and Weingand[6] showed that a yield of 69.4 percent was obtained by heating 10 gm. of potassium chlorate in quartz vessels at 479° C. for 8 hours. The results in glass vessels were lower—below 60 percent. The catalyzing agents aluminum foil, iron, copper, nickel, boric acid and potassium hydroxide, lowered the yields. Pieces of quartz in the glass vessels increased the yields. It was not possible to change all of the chlorate in any experiment without reducing. the yield. They recommend the heating of pure chlorate in quartz vessels without the addition of any other substance. They made no experiments with sodium chlorate.

CONCLUSIONS.

These experiments show that a yield of about 55 percent potassium perchlorate can be obtained by heating potassium chlorate at 480° to 550° C. for 30 minutes to 4 hours, depending upon the quantity of chlorate used. The lower the temperature, the longer the period of heating and the higher the temperature, the shorter the period. The greater the quantity of chlorate used the longer the period and the higher the temperature.

Sodium chlorate gives smaller yields of perchlorate than the potassium chlorate. In all cases it must be heated at lower temperatures and for shorter time, due to its instability.

No catalytic agent or addition substance was found which increased the perchlorate yield, and most of the things tried distinctly lowered it.

Glass surfaces had a harmful action, hence large quantities of chlorate should be used in each experiment whereby the relative surface of glass exposed is less.

[6] Zeit. Electrochem. 1921, 27, 1.

It seems impossible to prepare perchlorate cheaply by heat decomposition of chlorates.

It is definitely shown that Fowler and Grant were in error in their statement that perchlorate is produced by heating chlorate with silver oxide.

DISCUSSION.

F. A. LIDBURY[1]: It is a somewhat astonishing fact that a paper on this subject should quote the textbook equation

$$KClO_4 = KCl + 2O_2$$

Are the authors not aware of or have they not re-discovered the fact that this decomposition is by no means so simple as represented by the equation and that when perchlorates are heated chlorates may be formed?

F. C. MATHERS (*Communicated*): The formation of potassium chlorate by heat decomposition of potassium perchlorate was not an aim of this research, hence the reaction mentioned above was not directly considered. It is hoped that Mr. Lidbury will cite the literature reference to this reaction.

[1] Works Mgr., Oldbury Electro Chemical Co., Niagara Falls, N. Y.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 22, 1922, President Schlueder-berg in the Chair.

CHANGES IN THE ELECTRICAL CONDUCTIVITY OF VARNISHES DURING DRYING.[1]

By H. C. P. Weber.[2]

Abstract.

One of the causes of the failure of varnished coils, when apparently satisfactory materials are used, is brought to attention. During the drying of certain insulating varnishes, products of an acidic nature accumulate. The experimental results indicate that the accumulation of these low resistance materials decreases the resistance during the oxidation of the varnish, and as the accumulation of these products stops, owing to their partial removal by volatilization, the resistance increases. In each part of the test coil the total net heating effect was to increase the resistance in the heated portion, while the adjoining portion decreased in resistance with certain varnishes. [A. D. S.]

In the insulation of electrical machinery the use of varnished cloths, tapes, and finishing or impregnation with varnishes has found wide-spread and consistent use. A favorite procedure for the insulation of coils, for instance, consists in treating the cotton-covered winding with an asphaltic or with a baking varnish either before or after winding the coil.

The results obtained by this treatment are usually satisfactory, and a thoroughly dried varnish yields one of the best insulating materials known, namely, a fairly pliable skin, of high resistance and of considerable breakdown strength.

In scrutinizing varnishes for insulating purposes it is customary to examine the materials for gross impurities, acidity or other

[1] Manuscript received August 3, 1922.

[2] Research Department, Westinghouse Electric and Mfg. Co., E. Pittsburgh, Pa.

conducting substances, as to nature and amount of solvent and as to rate of drying. As a rule, little attention is paid to the components as long as the practical results obtained are satisfactory. Tests are usually accompanied by measurements of the resistance and breakdown strength of the raw varnish. In addition, test samples are thoroughly baked and dried, and the electrical and mechanical properties are examined. Cloth and paper treated with such var-

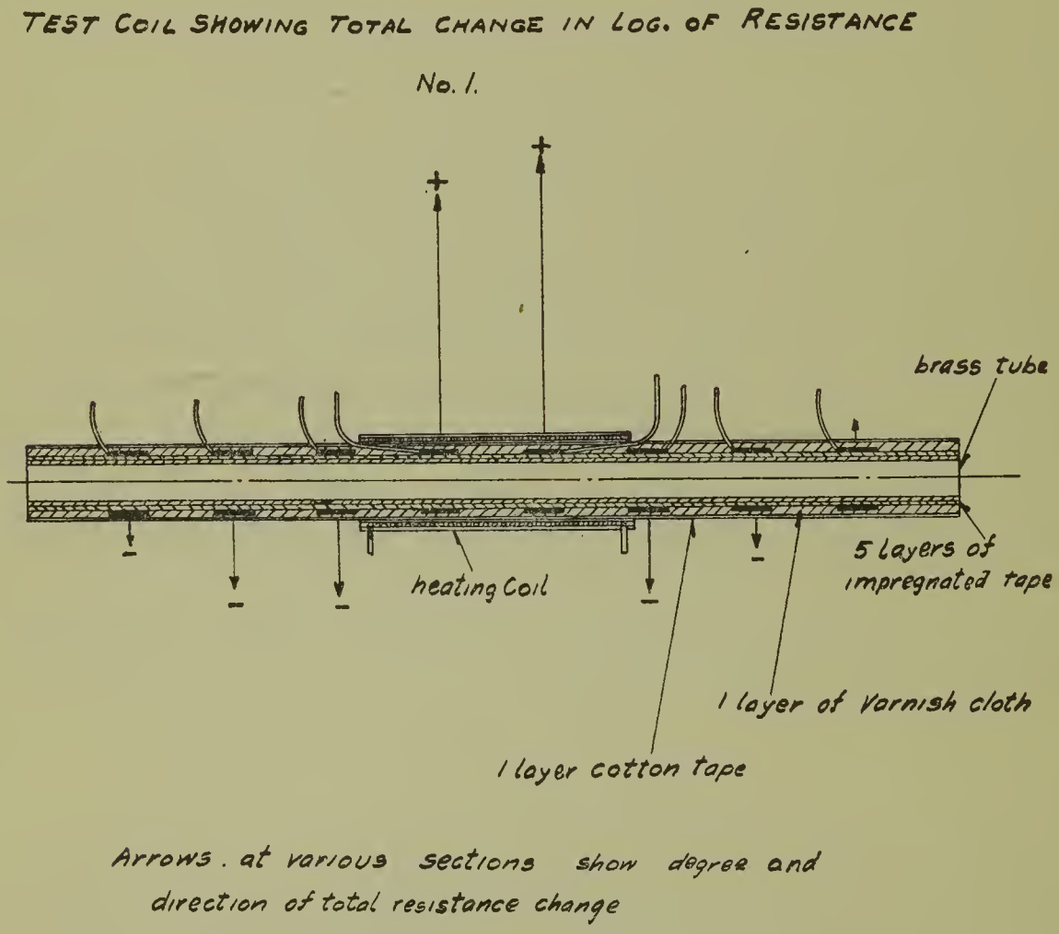

TEST COIL SHOWING TOTAL CHANGE IN LOG. OF RESISTANCE
No. 1.
brass tube
5 layers of impregnated tape
heating Coil
1 layer of Varnish cloth
1 layer cotton tape
Arrows at various sections show degree and direction of total resistance change

FIG. 1

nishes show resistances usually measured in megohms and breakdown strength of 8000 to 16000 volts per mil and even higher.

Nevertheless failures in varnished armature coils occur, which are puzzling in the light of the facts just mentioned. The purpose of this is to call attention to at least one of the causes of such failures when apparently satisfactory materials are being used.

In the process of drying of the oil varnish the hard film is produced by the absorption and combination of oxygen with the unsaturated oil. This is perfectly well known, and the fact has also been shown that during this oxidation a part of the original

fatty acid ester is split up. For the ordinary applications of varnishes as protective and beautifying coats these facts have no particular significance, and are only of theoretical interest.

When, however, the varnishes come to be used as insulating materials this "theoretical interest" becomes a practical problem.

Some time has been spent by us in an attempt to determine the nature and amount of the substances formed, their relation to the components of the varnishes examined, and their removal or suppression. They are acid in character, fairly good conductors in aqueous solutions, and fairly volatile. The essential feature for the electrical engineer is that they are initially absent in the varnish, and may with proper precautions be removed finally, but that there may be an intermediate condition in which the varnish is fairly well loaded with low resistance materials.

These materials are acidic in nature as was stated, but in order to avoid the necessity of distinguishing between acids which furnish appreciable hydrogen ion with water and such as do not, (for instance abietic acid of rosin, stearic, ricinoleic and similar substances) I have chosen to discuss the products forming during the drying of varnishes under the designation l o w r e s i s t a n c e m a t e r i a l s.

The present purpose is to give an experimental demonstration of the effect of these products upon the insulation resistance of varnished apparatus.

The accompanying diagram, Fig. 1, gives the essentials of the apparatus used. It consisted of

A. A thin brass tube 1 inch in diameter and 24 inches long. The tube was first wrapped with five layers of cotton tape overlapped at the edges. This tape wrapping was then brushed with the varnish to be tested until thoroughly saturated and was then set aside to air-dry and oxidize the varnish.

B. After taping and varnishing, eight electrodes of lead foil, each one an inch wide, were wrapped around the varnished cloth. These were equally spaced 3 inches apart and were provided with electrical connections. The interior brass tube constituted the opposite electrode, so that the insulation resistance of the varnished cloth could be measured at any one of the eight sections.

One layer of varnished tape and then a layer of plain white tape was wound over the varnish application and the electrodes.

C. A loosely fitting cylindrical heater, which could be slipped over the tube and covered the middle two electrodes, completed the arrangement.

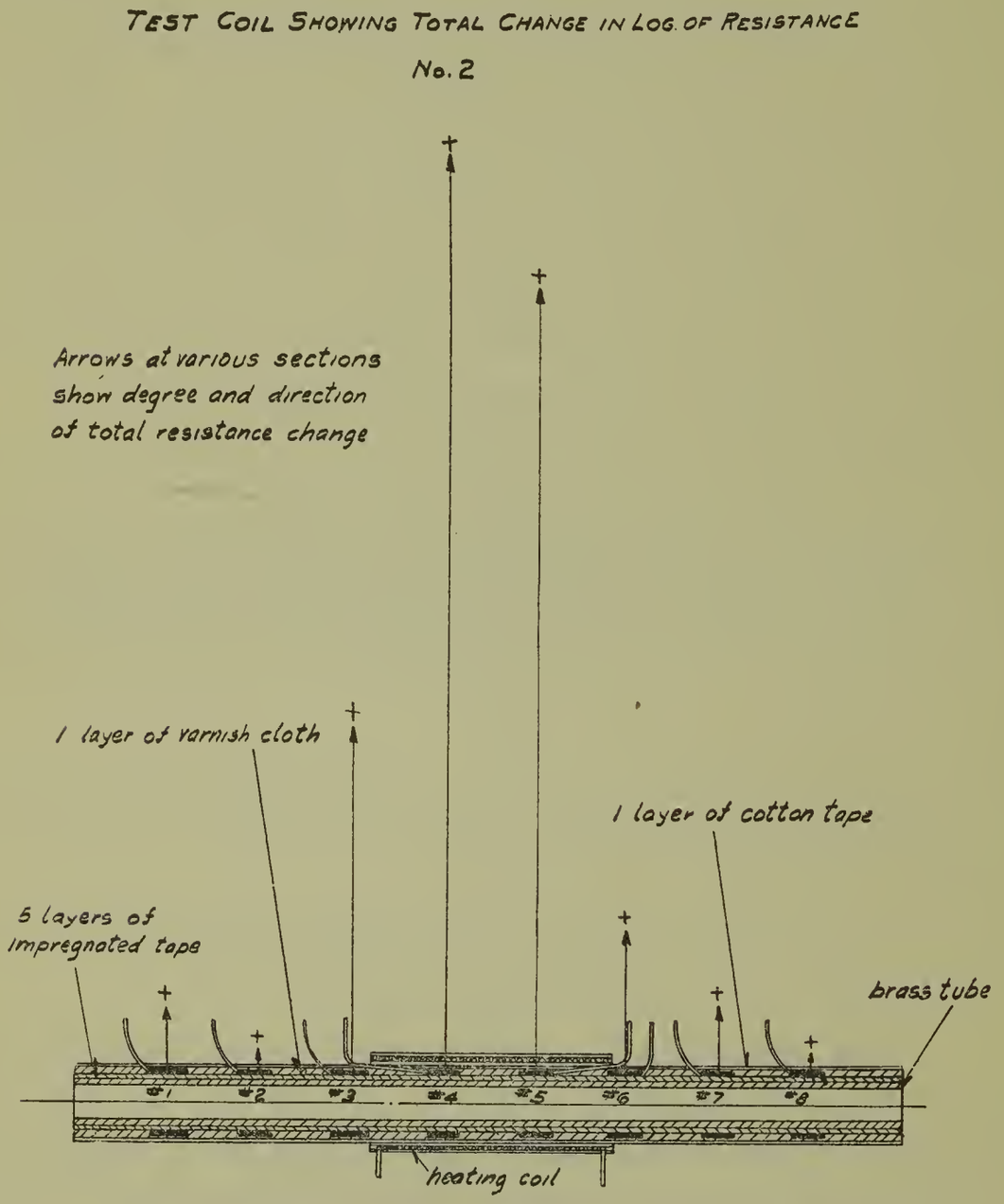


FIG. 2

Measurements were taken on these coils for 10 days. For the first five days, the coils were heated for a part of the day only, after that they were heated continuously, except for an hour a day to permit of readings of resistances at room temperature after cooling.

The two Figures 1 and 2, showing the arrangement of the

tests, also show the final results at the end of the heating period. The arrows show the direction and amount of change, plotted as logarithm of resistance. Thus the middle two sections of coil 1 each had a resistance of 1.05 and 1.3 megohms (at 95°C.), and

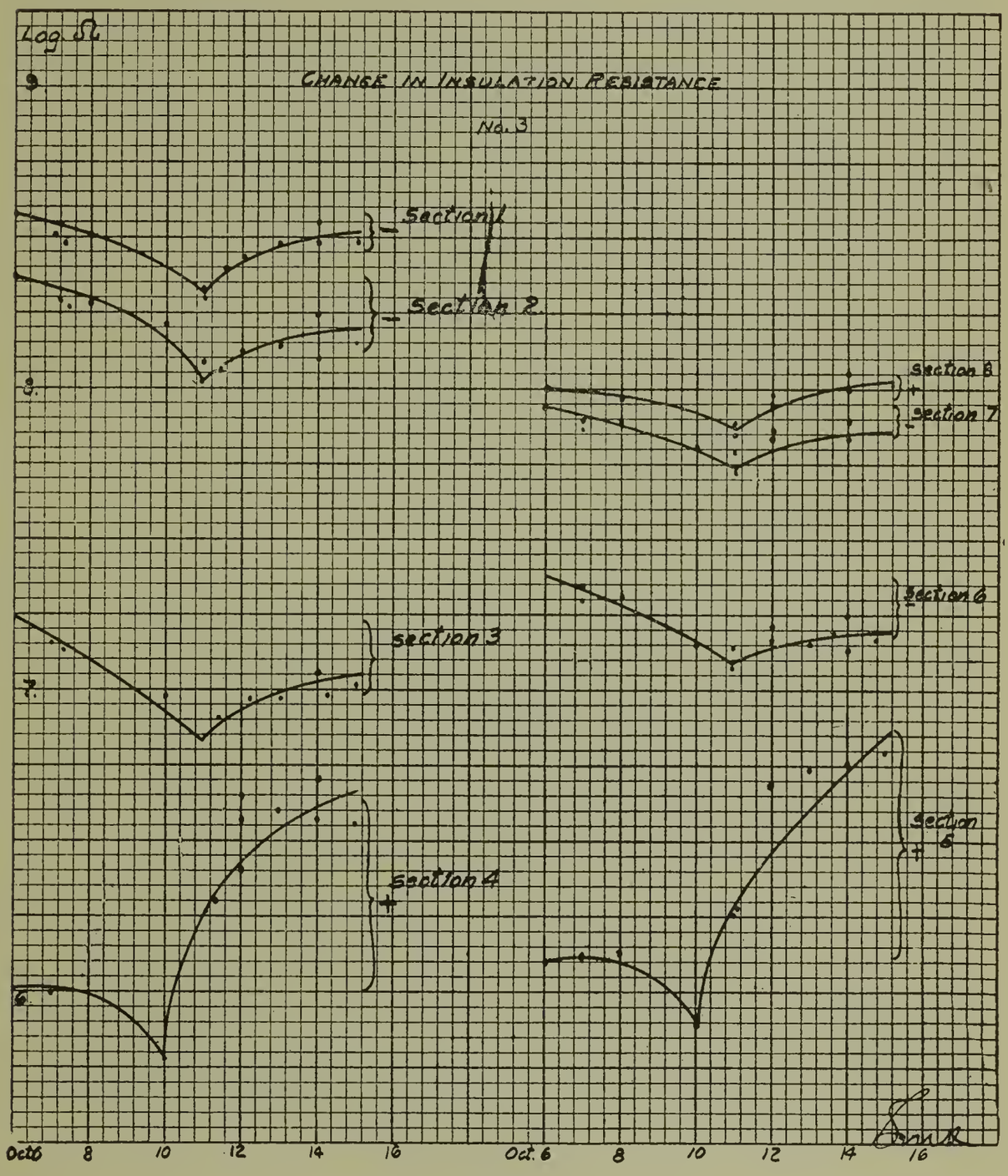


FIG. 3

during the course of heating this rose to 7 and 9 megohms (at 95°C.), measured through the insulation to the brass tube or ground. The adjoining sections at each side of these dropped from 18 and 25 megohms, respectively, to 13 and 18 megohms at

95°C. during the same period. Similarly the two sections 2 and 7 adjoining 3 and 6 dropped in resistance but less than the preceding. The two end sections show a slight change only.

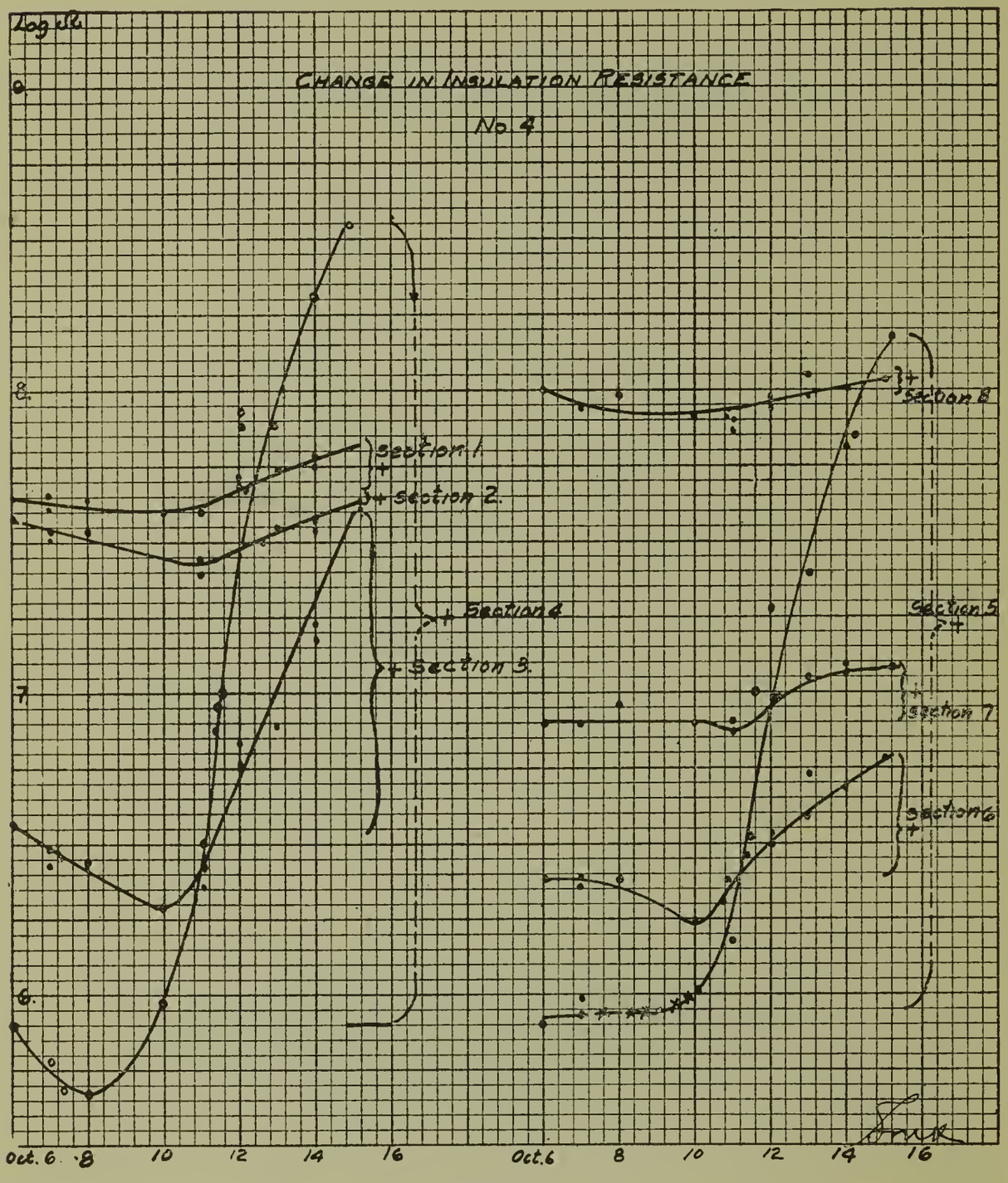


FIG. 4.

Fig. 2 shows a parallel test made under precisely the same conditions and at the same time as Fig. 1. The changes here are of an entirely different character, corresponding to the gradual seasoning and complete drying of the varnish. It is to be noted also that the final resistance obtained is much greater than in Fig. 1.

Figs. 3 and 4 show these changes more in detail, and with the daily variations indicated. Fig. 3 corresponds to Fig. 1 while Fig. 4 corresponds to Fig. 2. The curves are numbered to correspond to the sections in the preceding sketches, sections one and eight being the two end electrodes and section four and five the two at the middle.

The first thing to be noted is that, for the first four or five days, there is a steady decrease in the resistance. It is to be remembered that this effect is opposed to and is greatly overbalancing the normal drying out of the insulation which would increase the resistance. This decrease in resistance can only be due to the accumulation of l o w r e s i s t a n c e m a t e r i a l during the oxidation of the varnish. The accumulation of this low resistance material stops first in the heated portion of the coil, and from there on the resistance increases as these materials which have been shown to be slightly volatile are removed.

Shortly after the accumulation of low resistance material in the central portion of the test coil has reached its maximum, the adjoining sections also begin to increase in resistance but lag behind the hottest section. This lag is greatest in the portion adjoining the hot section. It is due to the accumulation of low resistance material driven over from sections 4 and 5 and is consequently greatest in the part indicated.

Fig. 4 shows a similar cycle with the varnish of a different type. This varnish differs in that it does not depend to any appreciable extent upon oxidation for its hardening and is shown for comparison.

The heated sections 4 and 5 show a slight original decrease in resistance, which is of much shorter duration and is followed by a steady and marked increase in resistance. This increase is due to the drying out of the insulation.

The adjoining sections 3 and 6 show a slight lag but soon overcome this and show a net increase in resistance, instead of a loss as with the preceding type. Furthermore, the sections adjoining the heated zone show the greatest increase in resistance, whereas in the preceding material they showed the greatest drop.

In every part of this coil the total net effect of heating the same was to increase the resistance.

CONCLUSIONS.

Certain types of varnishes are capable of developing substances of low electrical resistance during drying and oxidation.

These substances are acidic, slightly volatile and may be shifted about and accumulated by temperature differences.

In varnishes used for insulating purposes the amount of these substances formed during drying is of importance.

Further work is necessary to determine the relation between the amount of these low resistance materials formed and the composition of the varnish.

DISCUSSION.

G. S. WHITBY[1]: I would like to ask whether the acid that Dr. Weber isolated was soluble in water, and what was the nature of the resin or material employed.

H. C. P. WEBER: In answer to this question we may say that when we were first confronted with the difficulty we took various insulating materials singly, then jointly and in mixture. As a matter of fact, we found that we might use practically any resin and if it was finely distributed, say on a cloth base or on a tape of some sort, it would develop some acidity on exposure to air. This applies not only to resins such as rosin, copal, etc., but also to linseed oil, tung oil and practically every material that goes into the varnish. The amount of this acidity may be 3 percent and even more of a water soluble acid. I am speaking only about water soluble and volatile acids, because as far as the resistance is concerned the other acids might as well be neglected. Oleic acid, for instance, is a good insulator, so is abietic acid. Therefore it is only the water soluble acids that really are of interest in this connection.

There is one peculiarity which essentially locates the development of these materials with the varnish oils, and attention may be called to the fact that the amount of acidity is often in proportion to the amount of oil used in the varnish. There are also

[1] Dept. of Chem., McGill University, Montreal, Canada.

some characteristic results depending upon the kind of oil used. Linseed oil may develop acidity at a much greater rate than tung oil. As a matter of experience we believe we can take a linseed oil varnish and a tung oil varnish and distinguish between the two by means of the water soluble acid which is developed.

As to the proper and accurate methods for determining the acidity, for the sake of specifications and similar purposes, we are somewhat uncertain as yet, since we do not know the exact bearing of all the variables, of which there are quite a number.

F. W. ROBINSON[2]: I should like to ask Dr. Weber whether it is not important, in the application of these oil varnishes for electrical insulating purposes, that the layers of insulating material be put on very thin and be thoroughly dried before the next increment of varnish is applied? The processes involved are primarily oxidations by the air and incidental polymerization, and where a thick layer is involved, the drying of the lower portions of the layer is much retarded by the hardening of the upper surface.

I mention this point because recently I found a case of a firm that wanted to dry some oil varnishes very rapidly and they used a quartz mercury arc-lamp in order to accelerate this drying. With a fairly thick layer of varnish the outer coating of the varnish dried so rapidly under the ultra-violet light that it could be peeled off, leaving a layer of varnish underneath still liquid.

H. C. P. WEBER: Of course there is only one answer to that question, namely, the statement that the position taken is absolutely correct; but manufacturing is always a compromise between what we theoretically ought to do and production. It must be realized that when you make a coil, for instance, you may wish to put on 7, 8, or 10 layers. Consider the proposition of putting on 10 layers and drying each one thoroughly before you put on the next, from a manufacturing point of view. If a theoretically perfect job could be made, I think manufacturers attempting to do so would probably have to go out of business.

COLIN G. FINK[3]: It would take about three or four years to make an armature.

[2] Newark, N. J.
[3] Consulting Electrometallurgist, New York City.

HENRY HOWARD[4]: I would like to ask Dr. Weber if he can lay down any specifications as to how a generator or motor ought to be handled by the customer so that it survives these youthful diseases.

H. C. P. WEBER: A motor in its "childhood days" should be started in the way that it is going to go and kept going for some time. The bearing of this on the troubles mentioned is as follows: The varnish is oxidized and low resistance materials have accumulated; the motor is shipped and perhaps encounters conditions of unusual humidity. It is started in operation and run for 24 hours and possibly gets quite hot in one particular part of the motor, while some other portion of the motor is a great deal cooler. In the portion that has been cooler the low resistance material will be accumulated and the next time the motor is started there is a great likelihood that it will burn out.

F. M. TURNER, JR.[5]: I want to ask one simple question. Can anything be accomplished by aging motors, so to speak, before they are put on the market? For instance, manufacturing them a sufficient length of time ahead of when they are likely to be sold, so that these conditions become more or less static before the motor gets into the hands of the customer.

H. C. P. WEBER: If a motor could be made today, sold tomorrow and shipped the day after, nobody would run into this trouble. That is, the trouble is most likely to develop in aged motors which have not been run, because during the aging the oxidation products accumulate. When the motor has not run, these accumulations have not been driven out. They cannot be aged out at ordinary temperatures.

CARL HERING[6]: How about baking them?

H. C. P. WEBER: That can be done. They can be best driven out by moderate fairly continuous service. Such procedure carried out on the part of the manufacturer would practically be equivalent to a continued service test on every motor sent out and would naturally entail an additional expense in production of the

[4] Grasselli Chemical Co., Cleveland, Ohio.
[5] Technical Editor, Chemical Catalog Co., New York City.
[6] Consulting Electrical Engr., Philadelphia, Pa.

motor. The real solution of the difficulty lies in the proper selection of varnishes so that these injurious products are reduced to a minimum. While they can never be eliminated absolutely in this type of insulation, it is not impossible to obtain satisfactory results by the judicious selection of materials, and we believe it will be possible to eliminate the trouble in this manner.

C. G. SCHLUEDERBERG[7]: I think it is particularly gratifying to have pure research applied to manufacturing problems in this way. In listening to the discussion this morning on electric enameling furnaces, I was particularly impressed by the possibilities before the average electrical manufacturer, if he would only employ the services of an ordinary everyday garden variety of physical chemist. For instance, we listened to a discussion about saturation of vapor phase and equilibrium of reaction, which every physical chemist could have predicted right off the reel. Yet the manufacturer had to do a lot of elaborate testing and explosion, and other flub-dubery, when an ordinary graduate physical chemist would have known the facts beforehand.

This is a subject very close to home, and I only wish we could get the manufacturers of the country more generally interested in the advantage of research. However, I am hopeful, because I think the advantages of research and the employment of high grade chemists are becoming better appreciated every day.

[7] Asst. to Mgr., Supply Dept., Westinghouse Elec. & Mfg. Co., East Pittsburgh, Pa.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 22, 1922, President Schlueder-berg in the Chair.

ARC ACTION ON SOME LIQUID INSULATING COMPOUNDS.[1]

By C. J. Rodman.[2]

Abstract.

Liquids possessing high dielectric strength, which have low viscosity, comparatively high fire and flash points, have been subjected to the action of electric arc at and below the liquid surface. For comparative results in these tests a high voltage high-frequency generator having a maximum potential of 100,000 volts and a frequency of approximately 330,000 cycles was used to disrupt the oil contained within a convenient vessel, between two accurately adjustable ball electrodes.

Halogenated aliphatic and aromatic hydrocarbons, as well as mixtures of these with some mineral oils, were subjected to breakdown. Finely divided and highly non-conducting amorphous carbon, saturated and unsaturated hydrocarbons lower in the series, hydrochloric acid (from chlorinated compounds) and a number of gases were obtained. These gases consisted chiefly of hydrogen and unsaturates with small amounts of carbon monoxide, carbon dioxide, methane and nitrogen. With the increase of molecular weight of the homologue series, the paraffines show a corresponding decrease in gas evolution per kilowatt second of arc rupture. With an increase of halogenation of the oils a decrease in gas eliminated per kilowatt second arc rupture was noted. The normal amount of gas per kilowatt second obtained from a mineral oil was approximately 97 cc. whereas that volume obtained from a highly chlorinated oil was as low as 4.2 cc./kilowatt second. The gas obtained in the latter case is non-explosive in any proportion, when ignited with air mixtures.

The liquid dielectrics are apparently broken down by a temperature pressure effect of very short duration, rather than by the

[1] Manuscript received August 3, 1922.

[2] Research Chemist, Westinghouse Electric and Mfg. Co., E. Pittsburgh, Pa.

sympathetic vibration and rearrangement of compounds by high frequency alone. The data obtained in this research have practical application in the operation of such apparatus as transformers, circuit breakers and condensers.

Hemptinne[3] found that he could increase the molecular weight of a compound by subjecting it to the action of an electric current, providing the discharge acted simultaneously upon the liquid and gas phases. The yield was influenced by the current density, frequency of the current, gaseous pressure, temperature of the liquid and the discharge distance. Prolonged action of the discharge caused polymerization and a thickening of the mineral oils. For a given intensity of current, the quantity of substance transformed was a maximum for a definite distance of electric discharge; this maximum varies with the pressure.

Numerous methods have been devised to hasten chemical reaction by subjecting the vapor and gaseous phases of certain hydrocarbons to electrical discharge, thereby producing compounds lower in molecular weight. The Cherry synthetic gasoline process is illustrative of this kind of transformation[4]. P. Torche in discussing oil circuit-breakers shows the relation of breaking work and volume of gas produced per 100 Kv. A. by the disconnection of a large short-circuit load between one pair of contacts beneath the mineral oil surface.[5] In using a tension of 10 to 30 kilovolts, an arc duration of 0.12 to 0.33 sec., a switch energy of 8.4 to 231 kilowatts, he obtained 46.5 cc. of gas per Kw. sec. using switch oil. He found that the switch oil gases were composed of hydrogen, methane, heavy hydrocarbons, carbonic acid, oxygen and nitrogen. Little difference was found in the nature of the gas composition when using various mineral oils. His report of the findings of the Committee of Swiss Association of Electricians does not fully agree with the results obtained by the writer.

In a convenient form of laboratory apparatus, described later in this paper, liquid dielectrics were readily subjected to the action of high frequency discharge. Though some difficulty was expe-

[3] Bull. Soc. Chim. Belg., 26, 55—63.
[4] Trans. Am. Electrochem. Soc., 1917, 32, 345.
[5] Revue Gen. del'Electricite, 1918, 311-319, 343-348.

rienced at first in accurately measuring the arc energy of the high frequency discharge, it was, however, a most satisfactory method of studying the behavior of the arc, and of obtaining the high voltages necessary to rupture the high dielectric strengths of the compounds used. The arc energy is much smaller in this application, yet the results obtained are in close agreement with some practical tests on a small circuit breaker where the energy of disruption was approximately 2.5 Kw. sec. Here the gas evolution per Kw. sec. is large compared with that reported by Torche, for a similar liquid insulation medium. The power used between the electrodes of the oil gap varies between 0 and 16 watts, depending upon the electrode separation and the insulation value of the medium used. Approximately 10 percent of the energy input is dissipated in heating the oil gap apparatus and containing liquid. At a 50 mil separation of the electrodes 21.6 calories of arc energy are used in decomposing light transformer oil to produce one cc. of mixed gases.

DESCRIPTION OF THE HIGH-VOLTAGE, HIGH-FREQUENCY GENERATOR.

As shown in the accompanying diagram and sketch, Fig. 1, the generator consists of the following apparatus. An air cooled one-half Kv. A. transformer, having a ratio of 1 to 60, is employed for charging the condenser. When used with the rheostat on 110-volt, 60-cycle main, the secondary voltage can be varied between 1500 and 6600. This transformer is of the high magnetic leakage type, and requires no external reactance to prevent the spark gap from arcing. Connected directly across the high voltage terminals of the transformer is an oil condenser. The capacity of this condenser which embodies 5 sections of glass and copper plates in lectroseal oil can be varied between 0.003 and 0.0143 microfarads in four equal steps.

In series across the condenser terminals are the primary of the Tesla resonator, and a Rentschler mercury vapor spark gap. This completes the exciting and primary oscillation circuits. Mounted within and (with the exception of ground connection shown) carefully insulated from the primary of the Tesla coil, is the secondary or high voltage winding, the terminals of which go directly to the oil testing gap. The Tesla coil is a simple air core

transformer having a ratio of about 1 to 75. The primary consists of eight turns of heavy rubber covered cable on a drum 9 inches long, and has one layer of 600 turns of No. 28 D. C. C. wire, the turns being spaced about the thickness of the wire to cut

High Frequency Oil Testing Apparatus.

Sketch of Test Set Up.

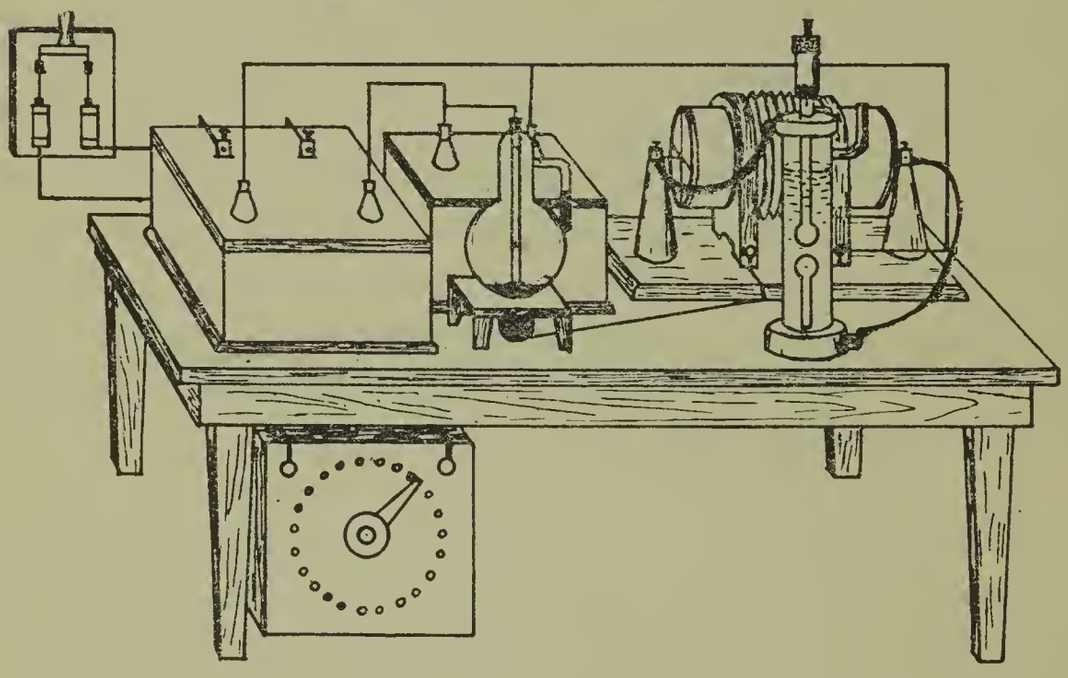


Diagram of Connections.

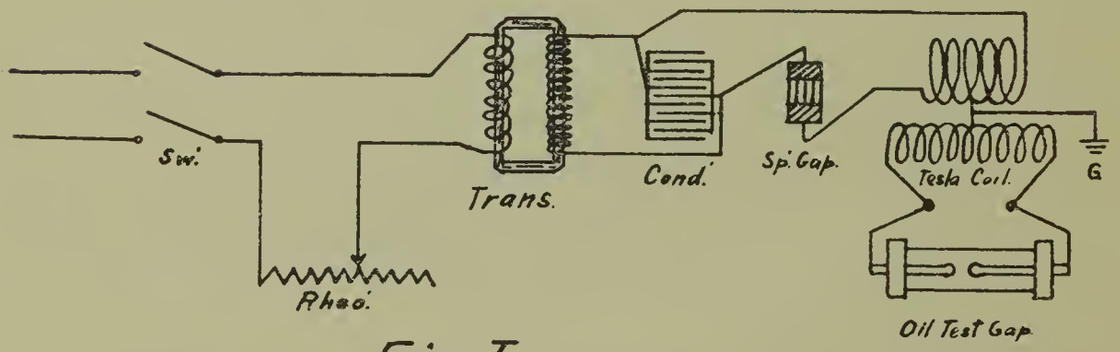


Fig I

down the distributed capacity. Both primary and secondary of this transformer are grounded at the middle points, thus effectively preventing surges of high voltage and frequency into the power circuits, and also maintaining a balance of potential difference in the testing circuit. The best results were obtained by using all of

the capacity available in the condenser when the frequency was approximately 330,000 and the maximum voltage 100,000.

It is well to note in connection with the Rentschler spark gap, that after a long run the length of the gap increases, due to the vaporization of the mercury, which condenses and runs back into the outer pool, which, being of larger diameter, does not rise in level as rapidly as the inner pool lowers. This raises the voltage and frequency slightly. The original conditions may, at the present time, be restored by shaking the bulb. Another bulb is being built in which the length of gap will be constant due to a special construction, which will allow the condensed mercury to run back into both pools.

The oil test cylinder, shown in Fig. 2, is essentially a glass receptacle for containing the liquid dielectric to be tested between two adjustable electrodes within the cylinder. The glass receptacle, of pyrex, is made of a 2-inch tube 12 inches long. The bottom end is constricted to a ¾-inch tube and is fitted into the heavy brass base by a glass-metal ground joint. A ¼-inch brass rod screwed centrally into the base projects upward into the glass receptacle about 2.5 inches. The top of the tester is similarly fitted with a brass cap having a long electrode reaching down into the cylindrical receptacle. Brass spheres ½-inch diameter are used as the electrode terminals. The distance between the spheres is readily regulated by movement of the upper electrode, and is read by having the electrode directly attached to a screw micrometer whereby a regulation of 0.0004-inch is quickly made. The upper and lower brass ends are electrically connected by means of heavy copper leads to the secondary of the Tesla coil. Little electrical leakage occurs under these conditions. A glass tube ¼-inch diameter serves as an outlet for the disrupted oil gas, vapors, and smoke. The volumes of gaseous products are conveniently read by a burette, accurately calibrated.

The test cylinder is filled approximately three-fourths full (about 250 to 300 cc.) of the liquid to be tested through the opening made by withdrawing the upper electrode and brass cap which fits as a stopper at the ground glass-metal joint. This amount of liquid is necessary so that the high voltage used does not admit of leakage over the surface of the liquid, through the glass and along the glass walls to the other electrode. The glass cylinder is made

about a foot long so that the surface of the liquid may be several inches above the gap. Breakdown has occurred over the surface of the liquid, puncturing the glass container, when the liquid was 2, 3 and even 4 inches deep above the ⅛-inch gap when using a good grade of mineral oil having a breakdown strength of 35 Kv. 1/10-inch gap.

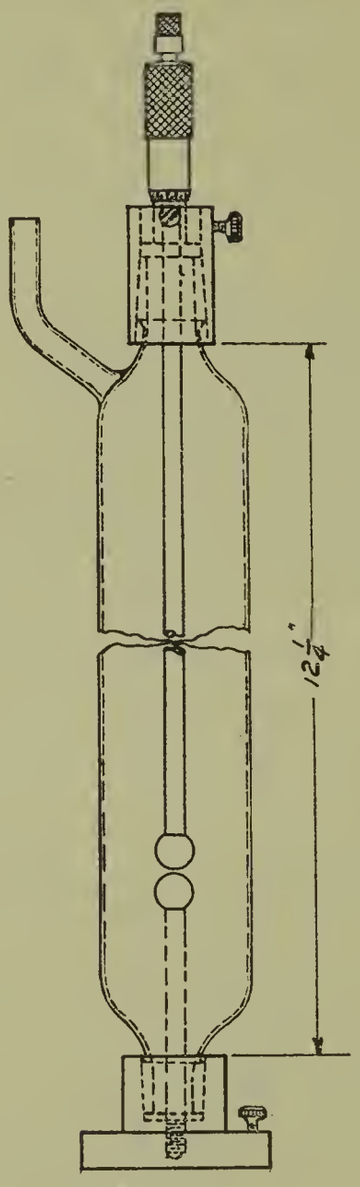


Fig II

Scale-Half Size

The energy efficiency is comparatively low with the apparatus shown in Fig. 2 above. Laboratory tests were found to work satisfactorily where the arc energy may be evaluated by calorimetric measurements, plus the energy supplied in the heats of decomposition of the compounds used, which result was checked against measurements of the energy input, and efficiencies of the

apparatus. For the production of gases commercially an apparatus of much greater efficiency must be provided. It is suggested also that very finely divided carbon black may be produced in oil by the action of a great number of small discharges under high voltage.

PRODUCTS OF ARC DISRUPTION OF OILS.

A great number of analyses of gases obtained from both the commercial circuit breaker and the oil gap have been made. Hydrocarbon oils of the general structure C_nH_{2n+2} are broken up into carbon dioxide (if any air or dissolved oxygen is present) unsaturated hydrocarbons, carbon monoxide, methane, ethane and hydrogen. An average analysis of a number of oil decomposition gases formed by high frequency discharge in transformer oil, is given in the table below.

TABLE I.

Average Analysis of Gases.

Oil	CO_2	Unsat.	O_2	CO	H_2	CH_4	N_2
N. Trans.	0.85	22.38	2.11	0.80	65.6	2.36	5.6
Lect. Oil	0.24	19.05	2.38	0.24	68.25	3.81	6.18

This table gives an analysis of oil decomposition of gases, which are the result of circuit breaker discharges in lectroseal oil. It is indeed interesting to note the close relationship in analyses of gases obtained by widely different sources of discharge. Because of the wide latitude of frequency in arc rupture, thus producing similar explosive gases, its use for starting motors or ignition systems is indeed valuable.

If the arcing process is permitted to run continuously, the oil at first appears brown, then soon becomes black. The color is due to myriads of very fine particles held in suspension within the oil. Careful examination of the particles showed that they were composed of amorphous carbon. The carbon is very finely divided, thus its use as carbon black or pigment is suggested.

This type of carbon is highly resistant to the passage of an electric current and does not lower the breakdown strength of the oil appreciably. Carbon precipitate of this character should not

be confused with the carbonaceous material found in an oil which may be an agglomerated mass of dirt particles and oxyasphaltic sludges. The latter are often found in oil due to admixture of accidental impurities with the oil or to oxidation products of the oil. While the oxyasphaltic sludges affect the insulation value more than does the amorphous carbon, both of these types have a much higher dielectric strength than do dust and dirt particles, which may line up under the stress of an electrical field to cause premature breakdown.

The liquid products of arc disruption represent but a small part of the reaction products. They are usually members of the same hydrocarbon series, but lower in molecular weight. Using a highly saturated paraffine oil only a small percentage of unsaturated compounds are found after three hours of continuous discharge within the oil.

It is interesting to observe the effect of the passage of an arc through oil. As the arc forces its way through the liquid it seems probable that it comes directly in contact with a liquid layer only a few molecules deep, that is, the temperature gradient between the active arc and the unchanged oil is exceedingly steep, so that the oil which is cracked is quite completely broken down. Immediately following the arc passage the carbon is left free in a reducing atmosphere, and much the greater part of the hydrogen is left in the elemental state. If the action of the arc cracked more than the immediate molecular layers, one would expect to find appreciable quantity of carbonaceous materials and unsaturated liquids similar to those found in actual hot spot decomposition experiments. Careful examination of the arced liquid paraffine oils does not show the presence of an appreciable quantity of cracked unsaturates.

GAS EVOLUTION PER KILOWATT-SECOND

The action of the high frequency discharge over varying arc gaps was observed in various liquids when placed in the test cup. A record was made of the electrode separation, the watts consumed, and the gas evolution per minute. Table II gives the data for Wemco A transformer oil, and is illustrative of the observations recorded on each liquid tested.

TABLE II.

Gas Evolution at Varying Arc Gaps

Electrode Separation in Mils	Watts	Gas Evolution per Min. cc.	Kw. Sec.	Gas/Kw. Sec. cc.
25	1.99	11.5	0.119	96.8
50	3.97	23.0	0.238	96.7
75	5.96	34.5	0.358	96.5
100	7.94	46.4	0.477	97.2
125	9.92	58.0	0.595	97.4

Average gas per Kw. sec = 96.9 cc.

Table III gives the gas evolution from various liquids per Kw. sec. of arc discharge. Wemco A, B, and C represent three grades of mineral oil, consisting mostly of C_nH_{2n+2} series where n equals 11 to 16. Wemco A is used for transformers. Wemco B, the oil of heavier molecular weight, is used for switch purposes. Wemco C is an oil of high flash characteristics, and is used in apparatus where the fire hazard is greatest. Reference to Figures 3 and 4 will indicate the trend of the curves showing the gas evolution of various liquid dielectrics, when subjected to the action of the high frequency arc at definite gap distances.

TABLE III.

Gas Evolution from Various Liquids

Substance	Gas Evolution 59 Mils Gap. cc.	Gas per Kw Sec. cc.
Gasoline 68°	27.0	113.3
Wemco A	21.9	92.1
Wemco B	19.5	81.9
Wemco C	17.5	72.7
Benzol	10.8	45.5
Monochlorbenzol	4.4	18.5
Orthodichlorbenzol	1.1	4.6
Dichlormethane	4.6	19.3
Chloroform	3.7	15.5
Carbon tetrachloride	1.0	4.2

There is a consistent decrease in gas evolution per Kw. sec. with the increase in molecular weight of the paraffines. In both the chlorinated aliphatics and aromatics there is a decided decrease in gas evolution per Kw. sec. as the halogenation increases. A

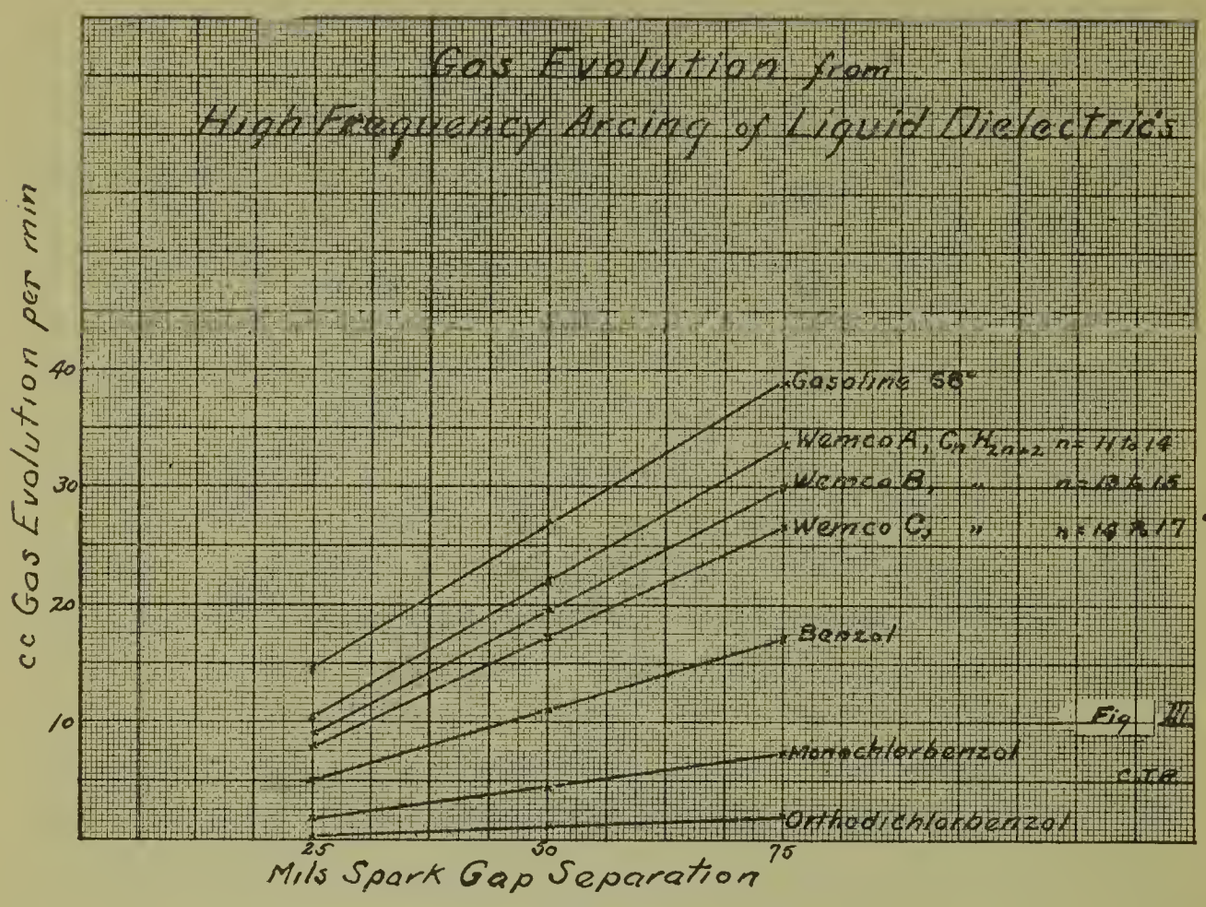

Gas Evolution from
High Freqeuncy Arcing of Liquid Dielectrics
cc Gas Evolution per min
40
30
20
10
Gasoline 58°
Wemco A, C_nH_{2n+2} n= 11 to 14
Wemco B, " n=13 to 15
Wemco C, " n=14 to 17
Benzol
Monochlorbenzol
Orthodichlorbenzol
Fig III
C.J.R.
25
50
75
Mils Spark Gap Separation

FIG. 3

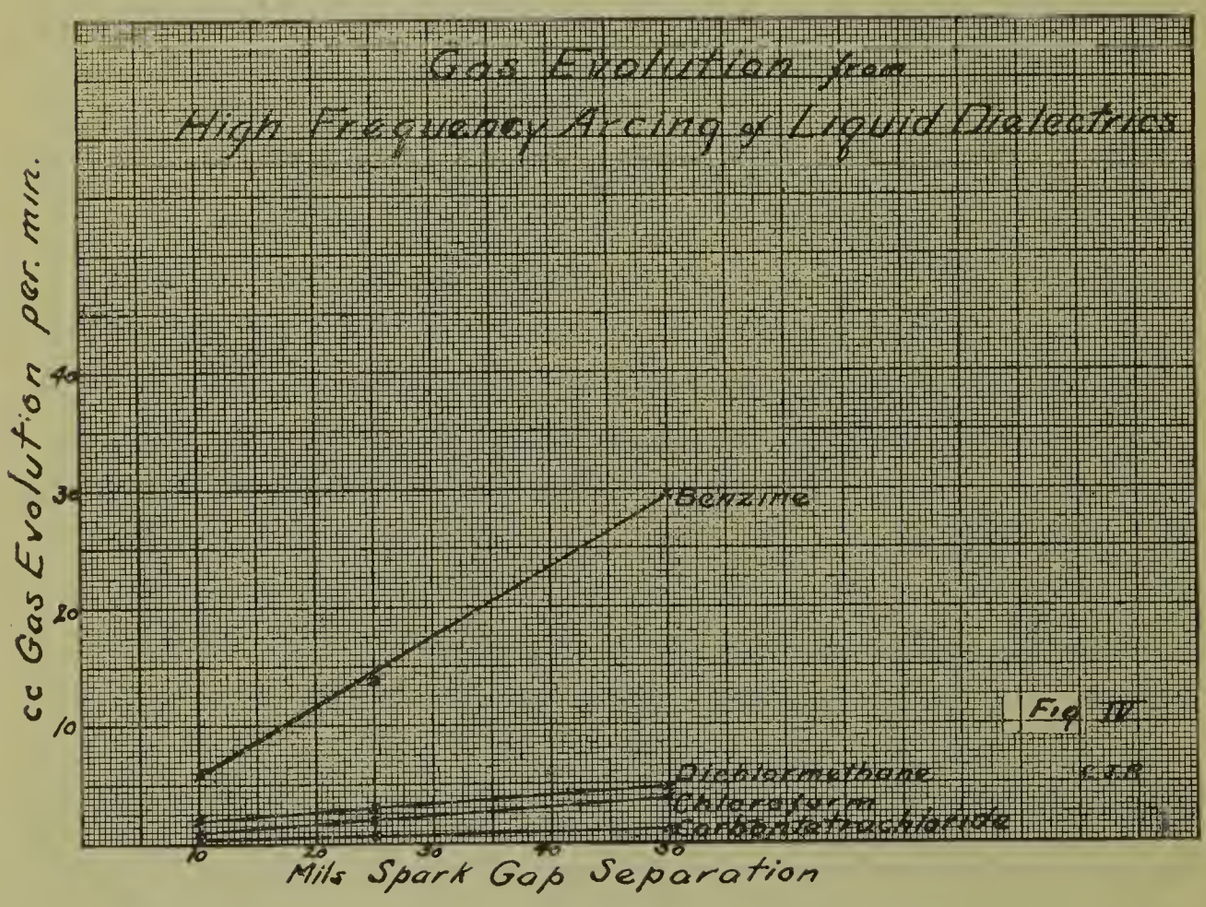

Gas Evolution from
High Frequency Arcing of Liquid Dielectrics
cc Gas Evolution per min.
40
30
20
10
Benzine
Dichlormethane
Chloroform
Carbontetrachloride
Fig IV
C.J.R.
10
20
30
40
50
Mils Spark Gap Separation

FIG. 4.

number of mixtures of mineral oils with halogenated compounds have been made and subjected to the arcing treatment. Liquids of comparatively high breakdown strength, having a very low gas evolution, and being practically non-inflammable have thus been produced for circuit breaker and oil switch application.

The disrupted oils not only give off gas but an appreciable quantity of unsaturates are formed, together with members of the same series lower in molecular weight and some free amorphous carbon. The dielectric strength of the oil mixture diminishes very slowly as the arcing process is continued. The carbon formed is readily separated by filtration and the oil is thereby brought back to its former insulation value. A sample of orthodichlorbenzol had an initial breakdown of 21 kilovolts at 0.1-inch gap. After continued arcing for an hour, it fell to a value of 11 Kv. It was then well shaken with MgO, CaO and a small quantity of filtchar and it was then filtered. The breakdown then tested 22 kilovolts. Switch oil may be similarly quickly rejuvenated.

The disruption of chlorinated oils by electrical breakdown gives an amount of chlorine and hydrochloric gas depending upon the chlorine concentration of the compound. CCl_4 or $C_6H_4Cl_2$ gives less than one-tenth the volume of gas per Kw. sec. upon disruption than does a switch oil (hydrocarbon oil) under similar treatment. Carbon tetrachloride alone breaks down into chlorine and very finely divided carbon. However, if CCl_4 is mixed with an appreciable quantity of hydrocarbon oil, then very little chlorine is given off, the carbon is very low, but the HCl concentration is increased. Similarly other chlorinated hydrocarbons having an appreciable quantity of H_2 in the molecule give hydrochloric acid instead of free chlorine. If the oil is kept dry, or given an occasional treatment with lime, it can be kept in a condition where the corrosion of the metallic parts is negligible.

In the apparatus described, the heating effect of continued high frequency discharge upon the oil ambient to the arc zone is very small indeed. The oil immediately surrounding the arc is only momentarily subjected to an appreciable rise in pressure as the arcing proceeds. It seems probable that the very thin layer of oil surrounding the arc zone suffers decomposition, and the great quantity of oil surrounding this thin layer remains unaltered chemically. It acts only as a medium in which the carbon is readily

dispersed and in which there is dissolved small quantities of lower saturates with some unsaturates. The oil quickly becomes loaded with the disrupted gases.

The gas evolution upon disruption is practically constant with time. Increasing the viscosity of the insulation medium very gradually decreases the gas evolution. Very viscous castor oil greatly retards the progress of the gas in its passage away from the arc zone. The gas is easily ionized and thus becomes a conductor which tends to make the arc hang on much longer. Where large loads are disconnected, as in circuit breakers where the high energy concentration plays in immediate contact with the liquid vapor phase, the gases are sent out into the oil with explosive violence. In this case the effect of viscosity is much less pronounced.

CONCLUSIONS.

A convenient high-voltage high-frequency generator for laboratory use has been described.

The gas evolution, the nature of the gas, and the amounts per Kw. sec. arc rupture of certain liquid dielectrics have been given.

There is a consistent decrease in gas evolution per Kw. sec. with the increase in molecular weight of the paraffines.

In both the halogenated aliphatics and aromatics there is a decided decrease in gas evolution per Kw. sec. as the halogenation increases.

The author wishes to express thanks to Paul Guest and J. E. Shrader for their assistance in constructing the apparatus and to James G. Ford and O. H. Eschholz who assisted in the experimental work.

DISCUSSION.

C. G. SCHLUEDERBERG[1]: I think we all appreciate that the question of oil circuit-breakers, and the behavior of the insulating oil or other substance used in the breakers, is of special importance, and will continue to be so in view of the large amounts of power

[1] Asst. to Manager, Supply Department, Westinghouse Electric & Mfg. Co., E. Pittsburgh, Pa.

being concentrated in single generating stations, as for instance at Queenston, Ontario, and elsewhere, and the necessity for the proper control of that power through circuit breakers of various kinds. In that connection there has been a great deal of research done, a great many tests have been made, and the behavior of the oil or other insulating medium used in these circuit-breakers is of particular interest and has been widely studied.

I do not know that any better dielectric material has been so far discovered than a good grade oil. Recent improvements have been along lines of ruggedness and high speed operation, and step by step instantaneous breaking of the current. I say "instantaneous" advisedly in that a fraction of a second, or a few seconds, may intervene, depending on the position of resistance or inductance between the successive steps in opening the circuit.

The subject is exceedingly vital and one which will continue to be of importance to engineers, chemists and electrochemists, as long as we use electric power.

COLIN G. FINK[2]: I would like to ask Mr. Rodman how much carbon tetrachloride is used nowadays? Is it actually displacing some of the heavy oils?

C. J. RODMAN: That depends on the design of the circuit-breaker. There are some products in reaction with carbon tetrachloride that give up hydrochloric acid, and if you can so construct the circuit-breaker as to get away from the corrosive action, you have quite an advantage in using carbon tetrachloride. In other respects carbon tetrachloride is very good.

COLIN G. FINK: It is just that point regarding corrosion that was brought to my attention.

C. J. RODMAN: In some types of circuit breakers, where the materials are primarily of copper and wood, we have used carbon tetrachloride successfully.

C. G. SCHLUEDERBERG: As a further point of interest in connection with the behavior of liquid insulators or similar compounds when exposed to the electric arc, I mention the use of fire extinguishers, which has been brought to popular attention lately in the daily newspapers, particularly around New York, in

[2] Consulting Electrometallurgist, New York City.

connection with the subway accident which occurred some weeks ago. The accident was followed by a panic on account of the development of noxious fumes after the alleged use of a certain fire extinguisher, which is supposed to contain carbon tetrachloride as its active principle. As a result of that accident, and the subsequent investigations, there has been widespread inquiry into the behavior of carbon tetrachloride, as well as other insulating compounds, when exposed to arc action, and not only arc action alone, but arc action in contact with certain materials, such as for instance charred insulation. The subject is one of a great deal of scientific interest and is of considerable industrial and general importance at the present time.

C. J. RODMAN: In this connection I may say that I left out some of the gaseous constituents that occur when halogenated hydrocarbons are disrupted by arc action. In this particular case pyrene was used, which is chiefly carbon tetrachloride. In that disruption there were formed small quantities of phosgene, some olefines, chlorine, acetylenes, some of which are particularly obnoxious.

C. G. SCHLUEDERBERG: Of course, when you get these gases in a confined space, such as a passenger car in a subway, naturally something is going to happen.

R. W. DAVIS, JR.[3]: In that connection it is interesting to note that one volume of carbon tetrachloride in about 500 volumes of air will extinguish a candle. That shows that carbon tetrachloride itself is rather dangerous.

[3] Jenkintown, Pa.

INDEX

PAGE

Abrams, Ralph B.—The Dezincification of Brass..... 39
Aldred, Jacob W. H. and Frank C. Mathers—Preparation of Perchlorates by Heating Chlorates.....285
Alley, J. D.—*Discussions*.....18 *et seq.*, 109 *et seq.*
Alloys at High Temperatures, Some Electrical Properties of—M. A. Hunter and A. Jones.....159
Alloys, Vacuum-Fused, of Electrolytic Iron with Carbon and Manganese, The Preparation and the Mechanical Properties of—Robert P. Neville and John R. Cain..... 21
Aluminium, A Simple Electric Crucible Furnace for Melting—A. Glynne Lobley 249
Application of Contractometer to the Study of Nickel Deposition, The —E. A. Vuilleumier 99
Arc Action on Some Liquid Insulating Compounds—C. J. Rodman....305
Bancroft, W. D.—*Discussions*.....95 *et seq.*, 108 *et seq.*, 213 *et seq.*
Bengough, G. D. and R. May—*Discussion*.....51 *et seq.*
Bisulphide, Carbon, Manufacture of—George A. Richter.....253
Blum, William—*Discussions*.....17 *et seq.*, 36, 59, 94 *et seq.*, 108
Brass, The Dezincification of—Ralph B. Abrams..... 39
Brophy, Oscar—*Discussion*.....240 *et seq.*
Cain, John R. and Robert P. Neville—The Preparation and the Mechanical Properties of Vacuum-Fused Alloys of Electrolytic Iron with Carbon and Manganese..... 21
Carbon and Manganese, The Preparation and the Mechanical Properties of Vacuum-Fused Alloys of Electrolytic Iron with—Robert P. Neville and John R. Cain..... 21
Carbon Bisulphide, Manufacture of—Geo. A. Richter.....253
Carbons, Resistor, Resistivities of Some Granular—Clyde E. Williams and Gordon R. Shuck.....181
Ceramics in Electric Furnaces, Firing of—E. L. Smalley.....209
Changes in the Electrical Conductivity of Varnishes During Drying—H. C. P. Weber.....293
Chlorates, Preparation of Perchlorates by Heating—Frank C. Mathers and Jacob W. H. Aldred.....285
Collins, E. F.—*Discussions*.....145 *et seq.*, 180
Collins, E. F.—Electric Heat, Its Generation, Propagation and Application to Industrial Processes.....113
Compounds, Liquid Insulating, Arc Action on Some—C. J. Rodman..305
Conductivity, Electrical, of Varnishes During Drying, Changes in the—H. C. P. Weber.....293

PAGE
Contractometer, The Application of, to the Study of Nickel Deposition —E. A. Vuilleumier..... 99
Davis, R. W., Jr.—*Discussions*.....268, 318
Definitions, Two, Electrosmosis and Electrophoresis—Oliver C. Ralston 269
Development of Industrial Electric Heating for Low Temperature Enameling—Wirt S. Scott.....195
Dezincification of Brass, The—Ralph B. Abrams..... 39
Diffusion of Electrodeposits into Zinc, Electroplated Zinc and the—Walter G. Traub..... 55
Effect of Heat Treatment on the Hardness and Microstructure of Electrolytically Deposited Iron—Norman B. Pilling..... 9
Effect of Impurities in Nickel Salts Used for Electrodeposition, The—M. R. Thompson and C. T. Thomas..... 79
Effect of Single Impurities on the Electrodeposition of Zinc from Sulphate Solutions, The—John T. Ellsworth..... 63
Electrical Conductivity of Varnishes During Drying, Changes in the—H. C. P. Weber.....293
Electric Crucible Furnace, A Simple, for Melting Aluminium—A. Glynne Lobley.....249
Electric Heat, Its Generation, Propagation and Application to Industrial Processes—E. F. Collins.....113
Electrical Properties of Alloys at High Temperatures, Some—M. A. Hunter and A. Jones.....159
Electric Furnaces, Firing of Ceramics in—E. L. Smalley.....209
Electric Steam Generators and Their Application—P. S. Gregory.....215
Electrodeposition of Zinc from Sulphate Solutions, The Effect of Single Impurities on the—John T. Ellsworth..... 63
Electrodeposition, The Effect of Impurities in Nickel Salts Used for—M. R. Thompson and C. T. Thomas..... 79
Electrolytically Deposited Iron, Effect of Heat Treatment on the Hardness and Microstructure of—Norman B. Pilling..... 9
Electrolytic Iron with Carbon and Manganese, The Preparation and the Mechanical Properties of Vacuum-Fused Alloys of—Robert P. Neville and John R. Cain..... 21
Electrolytic Oxidation of Isoeugenol—Alexander Lowy and Catherine M. Moore.....273
Electrophoresis and Electrosmosis, Two Definitions—Oliver C. Ralston 269
Electroplated Zinc and the Diffusion of Electrodeposits into Zinc—Walter G. Traub..... 55
Electrosmosis and Electrophoresis, Two Definitions—Oliver C. Ralston.269
Ellsworth, John T.—The Effect of Single Impurities on the Electrodeposition of Zinc from Sulphate Solutions..... 63
Enameling, The Development of Industrial Electric Heating for Low Temperature—Wirt S. Scott.....195

PAGE
Falter, P. H.—*Discussion*.....229 *et seq.*
Fink, Colin G.—*Discussions*
18 *et seq.*, 37, 51, 94, 178 *et seq.*, 266 *et seq.*, 301, 317
Finkeldey, W. H.—*Discussion*..... 60 *et seq.*
Firing of Ceramics in Electric Furnaces—E. L. Smalley.....209
FitzGerald, F. A. J.—*Discussion*.....194
Forty-second General Meeting, Proceedings of..... 1
Furnace, A New Induction—J. Murray Weed.....233
Furnace, A Simple Electric Crucible, for Melting Aluminium—A. Glynne Lobley..... 249
Furnace Design, High Temperature, Principles of—E. L. Smalley.....147
General Meeting, Forty-second, Proceedings of..... 1
Generators, Electric Steam, and Their Application—P. S. Gregory.....215
Granular Resistor Carbons, Resistivities of Some—Clyde E. Williams and Gordon R. Shuck.....181
Gregory, P. S.—*Discussion*.....231 *et seq.*
Gregory, P. S.—Electric Steam Generators and Their Application....215
Guests Registered at Forty-second General Meeting..... 6
Hardness and Microstructure of Electrolytically Deposited Iron, Effect of Heat Treatment on the—Norman B. Pilling..... 9
Harvey, W. G.—*Discussions*.....178, 228 *et seq.*, 245
Heat, Electric, Its Generation, Propagation and Application to Industrial Processes—E. F. Collins.....113
Heat Treatment, Effect of, on the Hardness and Microstructure of Electrolytically Deposited Iron—Norman B. Pilling..... 9
Hering, Carl—*Discussions*.....36, 228, 242 *et seq.*, 245, 302
High Temperature Furnace Design, Principles of—E. L. Smalley....147
High Temperatures, Some Electrical Properties of Alloys at—M. A. Hunter and A. Jones.....159
Howard, Henry—*Discussions*.....18, 302
Hughes, W. E.—*Discussions*.....19 *et seq.*, 96 *et seq.*, 110 *et seq.*
Hunter, M. A. and A. Jones—Some Electrical Properties of Alloys at High Temperatures.....159
Hunter, M. A.—*Discussions*.....178 *et seq.*, 267 *et seq*
Impurities in Nickel Salts Used for Electrodeposition, The Effect of—M. R. Thompson and C. T. Thomas..... 79
Impurities, Single, The Effect of, on the Electrodeposition of Zinc from Sulphate Solutions—John T. Ellsworth..... 63
Induction Furnace, A New—J. Murray Weed.....233
Industrial Electric Heating for Low Temperature Enameling, The Development of—Wirt S. Scott.....195
Insulating Compounds, Liquid, Arc Action on Some—C. J. Rodman....305
Iron, Electrolytically Deposited, Effect of Heat Treatment on the Hardness and Microstructure of—Norman B. Pilling..... 9

PAGE
Iron, Electrolytic, with Carbon and Manganese, The Preparation and the Mechanical Properties of Vacuum-Fused Alloys of—Robert P. Neville and John R. Cain..... 21
Isoeugenol, Electrolytic Oxidation of—Alexander Lowy and Catherine M. Moore.....273
Jones, A. and M. A. Hunter—Some Electrical Properties of Alloys at High Temperatures.....159
Lidbury, F. A.—*Discussions*.....142, *et seq.*, 226 *et seq.*, 230 *et seq.*, 291
Liquid Insulating Compounds, Arc Action on Some—C. J. Rodman....305
Lobley, A. Glynne—A Simple Electric Crucible Furnace for Melting Aluminium 249
Lof, E. A.—*Discussion*.....223
Low Temperature Enameling, The Development of Industrial Electric Heating for—Wirt S. Scott.....195
Lowy, Alexander and Catherine M. Moore—Electrolytic Oxidation of Isoeugenol 273
Lowy, Alexander—*Discussion*.....284
Manganese and Carbon, The Preparation and the Mechanical Properties of Vacuum-Fused Alloys of Electrolytic Iron with—Robert P. Neville and John R. Cain..... 21
Manufacture of Carbon Bisulphide—Geo. A. Richter.....253
Mathers, F. C.—*Discussion*.....291
Mathers, Frank C. and Jacob W. H. Aldred—Preparation of Perchlorates by Heating Chlorates.....285
May, R. and G. D. Bengough—*Discussion*.....51 *et seq.*
McKay, R. J.—*Discussions*.....59 *et seq.*, 95
Mechanical Properties, and the Preparation, of Vacuum-Fused Alloys of Electrolytic Iron with Carbon and Manganese—Robert P. Neville and John R. Cain..... 21
Members Registered at Forty-second General Meeting..... 5
Microstructure and Hardness of Electrolytically Deposited Iron, Effect of Heat Treatment on the—Norman B. Pilling..... 9
Miller, Dwight D.—*Discussion*.....194
Moore, Catherine M. and Alexander Lowy—Electrolytic Oxidation of Isoeugenol 273
Neville, Robert P. and John R. Cain—The Preparation and the Mechanical Properties of Vacuum-Fused Alloys of Electrolytic Iron with Carbon and Manganese..... 21
Neville, R. P.—*Discussion*..... 37
Nickel Deposition, The Application of Contractometer to the Study of —E. A. Vuilleumier..... 99
Nickel Salts, The Effect of Impurities in, Used for Electrodeposition—M. R. Thompson and C. T. Thomas..... 79
Oxidation, Electrolytic, of Isoeugenol—Alexander Lowy and Catherine M. Moore.....273

PAGE
Perchlorates, Preparation of, by Heating Chlorates—Frank C. Mathers and Jacob W. H. Aldred....285
Pilling, Norman B.—*Discussions*....17 *et seq.*, 37
Pilling, Norman B.—Effect of Heat Treatment on the Hardness and Microstructure of Electrolytically Deposited Iron.... 9
Preparation and the Mechanical Properties of Vacuun-Fused Alloys of Electrolytic Iron with Carbon and Manganese, The—Robert P. Neville and John R. Cain.... 21
Preparation of Perchlorates by Heating Chlorates—Frank C. Mathers and Jacob W. H. Aldred....285
Principles of High Temperature Furnace Design—E. L. Smalley....147
Proceedings of the Forty-second General Meeting.... 1
Properties of Alloys at High Temperatures, Some Electrical—M. A. Hunter and A. Jones....159
Ralston, Oliver C.—Electrosmosis and Electrophoresis, Two Definitions 269
Reeve, A. G.—*Discussion*.... 60
Resistivities of Some Granular Resistor Carbons—Clyde E. Williams and Gordon R. Shuck....181
Richter, Geo. A.—*Discussion*....266 *et seq.*
Richter, Geo. A.—Manufacture of Carbon Bisulphide....253
Robinson, F. W.—*Discussion*....301
Rodman, C. J.—Arc Action on Some Liquid Insulating Compounds...305
Rodman C. J.—*Discussion*....317 *et seq.*
Ryan, F. J.—*Discussion*....143 *et seq.*
Saunders, L. E.—*Discussions*....142, 212 *et seq.*
Schluederberg, C. G.—*Discussions*....208, 267, 303, 316 *et seq.*
Scott, Wirt S.—*Discussions*....140 *et seq.*, 208
Scott, Wirt S.—The Development of Industrial Electric Heating for Low Temperature Enameling....195
Seede, J. A.—*Discussion*....244
Shuck, Gordon R. and Clyde E. Williams—Resistivities of Some Granular Resistor Carbons....181
Smalley, E. L.—Firing of Ceramics in Electric Furnaces....209
Smalley, E. L.—Principles of High Temperature Furnace Design....147
Smith, Acheson—*Discussion*....232
Some Electrical Properties of Alloys at High Temperatures—M. A. Hunter and A. Jones....159
Stansfield, A.—*Discussion*....213
Steam Generators, Electric, and their Application—P. S. Gregory....215
Sulphate Solutions, The Effect of Single Impurities on the Electrodeposition of Zinc from—John T. Ellsworth.... 63
Thomas, C. T. and M. R. Thompson—The Effect of Impurities in Nickel Salts Used for Electrodeposition.... 79
Thompson, M. R. and C. T. Thomas—The Effect of Impurities in Nickel Salts Used for Electrodeposition.... 79

PAGE
Thompson, M. R.—*Discussions*.....97, 111 *et seq.*
Traub, Walter G.—Electroplated Zinc and the Diffusion of Electrodeposits into Zinc..... 55
Turner, F. M., Jr.—*Discussion*.....302
Vacuum-Fused Alloys of Electrolytic Iron with Carbon and Manganese, The Preparation and the Mechanical Properties of—Robert P. Neville and John R. Cain..... 21
Varnishes During Drying, Changes in the Electrical Conductivity of —H. C. P. Weber.....293
Vuilleumier, E. A.—The Application of Contractometer to the Study of Nickel Deposition..... 99
Watts, O. P.—*Discussion*.....52 *et seq.*
Weber, H. C. P.—Changes in the Electrical Conductivity of Varnishes During Drying.....293
Weber, H. C. P.—*Discussions*.....193 *et seq.*, 300 *et seq.*
Weed, J. Murray—A New Induction Furnace.....233
Weed, J. Murray—*Discussion*.....244 *et seq.*
Weiser, F. S.—*Discussions*.....51, 180
Whitby, G. S.—*Discussions*.....267, 300
Williams, Clyde E. and Gordon R. Shuck—Resistivities of Some Granular Resistor Carbons.....181
Williams, H. M.—*Discussions*.....18, 59
Wilson, J. Rattray—*Discussion*.....244 *et seq.*
Zinc, Electroplated, and the Diffusion of Electrodeposits into Zinc—Walter G. Traub..... 55
Zinc, The Effect of Single Impurities on the Electrodeposition of, from Sulphate Solutions—John T. Ellsworth..... 63

PERIODICAL